An azido-bridged disc-like heptanuclear cobalt(II) cluster: towards a single-molecule magnet†

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A disc-like heptanuclear Co(II)-cluster, $[Co_7(bzp)_6(N_3)_9(CH_3O)_3]\cdot 2ClO_4\cdot 2H_2O$ (1) (bzp = 2-benzoyl pyridine), mixed-bridged by 3/4 azides ($\mu_{1,1}$ and $\mu_{1,1,1}$) and 1/4 $\mu_{1,1,1}$-methanol, shows slow relaxation at static zero and non-zero fields below 6 K, towards single molecule magnet behavior.

Research on single-molecule magnets (SMMs) has been one of the most active fields in the past decade, and is still rapidly expanding. SMMs not only show dramatic architectures, but also provide almost ideal systems for investigating the coexistence of classic and quantum effects, and are hopeful for applications in information storage and quantum computing in the future.[1–3] To date, great efforts have been mainly made on oxo-bridged Mn(III)- or Fe(III)-based SMMs,[1,2] and cyano-bridged heterometallic SMMs have become another increasing family.[3]

As a large anisotropic ion, Co(II) might be another possible candidate ion for SMMs, and its strong Ising-type anisotropic contribution has been demonstrated in some single-chain magnets (SCMs),[4] However, among the abundant Co(II)-based clusters,[5–7] only a few behave as SMMs.[7] One of the reasons might be the absence of effective ferromagnetic (F) coupling to give a large ground state, as oxo-bridges are inclined to mediate antiferromagnetic (AF) interactions. Recently, azido-bridged clusters have been exploited as new SMMs for end-on (EO) azido bridges, which is propitious to F coupling.[4b,6] Unfortunately, even for the ferro- or ferrimagnetic-like Co(II)-clusters resulting from partial substitution of OR^- by azide, SMM behavior was still not observed above 2 K, or even down to 40 mK.[1b,7] Thus it is still a big challenge in discovering the ingredients for Co(II)-based SMMs at present. Recently, we synthesized two well-isolated tape-like copper–azido compounds by choosing 2-benzoyl pyridine (bzp) as a terminal co-ligand.[8] Herein, using the same terminal ligand we acquired a novel disc-like heptanuclear Co(II)-based cluster, $[Co_7(bzp)_6(N_3)_9(CH_3O)_3]\cdot 2ClO_4\cdot 2H_2O$ (**1**), containing 3/4 azido ($\mu_{1,1}$ and $\mu_{1,1,1}$) and 1/4 $\mu_{1,1,1}$-methoxy bridges. The magnetic study suggested a dominant intra-molecular F coupling, and slow relaxation of magnetization.

The reaction of NaN_3 with $Co(ClO_4)_2\cdot 6H_2O$ and bzp in 6 : 5 : 5 molar ratio‡ in methanol solution yielded red plate-like crystals of **1**, belonging to monoclinic space group *C*2/*c*.§ **1** consists of an azido/methoxy bridged cationic heptanuclear cluster $[Co_7(bzp)_6(N_3)_9(CH_3O)_3]^{2+}$ and counter anions $[ClO_4]^-$ (Fig. 1). There are four independent Co^{II} ions, each assuming a distorted octahedral geometry with N–Co–N(O) angles in the range of 76–96° and Co–N(O) bonds of 2.08–2.18 Å. The disc-like core of nearly S_6 symmetry can be described as a $[Co_6]$ ring (Co1, Co2, Co3 and their centrosymmetric equivalents) plus Co4, which lies on the inversion centre. It is of note that the structural motif belongs to the increasing $[M_7]$ family, for which no $[Co_7]$ member has been reported until now.[9] Each ring Co^{II} ion chelated by one bzp ligand is linked to a neighboring one by one EO-azido group, and an up-down $\mu_{1,1,1}$-azido/OCH_3 bridge, which is simultaneously shared by the central Co4. Like other $[M_7]$ clusters, the structure is represented by a closest-packing arrangement of donor nitrogen/oxygen and Co atoms. All the outer EO-azido bridges are almost linear with $\angle$N–N–N $\approx 179°$, while only two μ_3 sites are occupied purely by azide groups (N13 and N13A) with $\angle$N–N–N $\approx 173°$, and the other four sites are co-occupied by azide (30%, $\angle$N–N–N $\approx 165°$) and methoxy (70%, C–O = 1.39 Å). The Co–N/O–Co angles are in the range of 96.2–100.5°, and the adjacent Co···Co distances are 3.17–3.22 Å. As shown in Fig. S0, ESI,† the clusters with two different orientations are well isolated by bzp with the nearest intercluster Co···Co distance of 7.8 Å.

The variable-temperature dc magnetic susceptibility of **1** (per $[Co_7]$ unit) is shown in Fig. 2.¶ The $\chi_M T$ value of *ca.* 22.4 cm^3 mol^{-1} K at 300 K, is much higher than the spin-only value of seven high-spin Co^{II} ions (13.1 cm^3 mol^{-1} K), indicating significant orbital contributions of the distorted octahedral Co^{II} ions.[10] Upon cooling, the value increases to a maximum of 63.8 cm^3 mol^{-1} K at 14 K, then decreasing sharply, where the sudden decrease might be mainly attributed to the presence of zero-field splitting (ZFS), as the *M*–*T* curve at 20 Oe showed a similar behavior to exclude a field saturation effect (inset of Fig. 2).

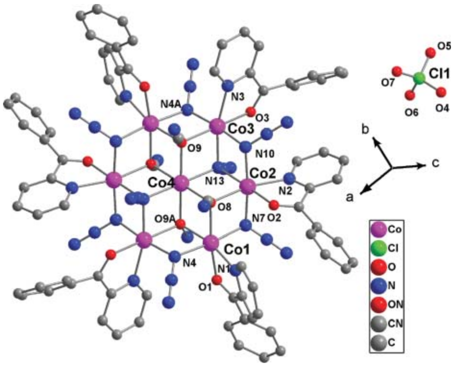

Fig. 1 The heptanuclear structure of **1** with atom-labeling.

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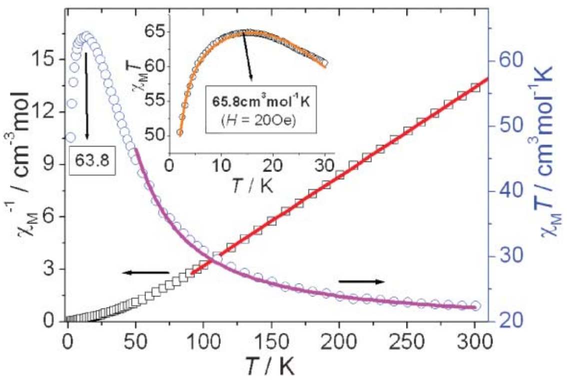


Fig. 2 Temperature dependence of $\chi_M T$ and χ_M^{-1} of **1** at an applied field (H) of 1 kOe. Inset: FCM at H = 20 Oe and 2–30 K. The solid lines represent the best fit to the Curie–Weiss law (red), the calculated magnetic susceptibilities by MAGPACK (purple), and the best fit to a S_6 symmetric heptanuclear model with each S_{Co}' = 1/2 (orange).

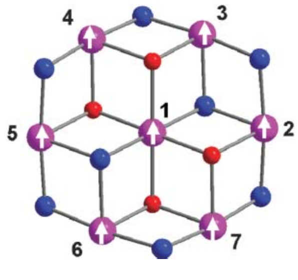
The data above 100 K obeys the Curie–Weiss law with C = 19.5 cm^3 mol^{-1} K and θ = +37.3 K, which clearly suggests an overall F coupling between the Co(II) ions within the cluster.

As there is a lack of an appropriate analytical expression of an anisotropic model for this complicated system, here, we attempted to approximate statistically the magnetic susceptibility of **1** by a S_6 symmetric heptanuclear model with isotropic g factor and an identical isotropic coupling constant (J_{intra}) (Scheme 1), where the exchange Hamiltonian is:

$$H = -2J_{\mathrm{intra}}\left(\sum_{i=2}^{7} S_1\cdot S_i + \sum_{j=2}^{6} S_j\cdot S_{j+1} + S_2\cdot S_7\right) + g_0\mu_B H_0 \sum_{i=1}^{7} S_i^z \quad (1)$$

A rough estimation by MAGPACK[11] gives J_{intra} = +3.5 cm^{-1} with each S_{Co} = 3/2 and g = 2.7 (Fig. 2). Compared with our previous compound Co(bt)(N$_3$)$_2$ (bt = 2,2′-bithiazoline),[4b] the decrease of the coupling interaction through the EO-azido bridges presumably originates from the smaller ∠Co–N–Co bridge angles. Otherwise, the Co^{II} ion is usually treated as an effective spin S_{Co}' = 1/2 center at low temperature.[10] Thus, a S_6 symmetric heptanuclear copper(II)-like model through Kambe's method[12] was simply used for simplicity with the energy expression:

$$E(S_{ij}) = -J_{\mathrm{intra}}\left(\sum_{i=2}^{7} S_{1i}(S_{1i}+1) + S_{23}(S_{23}+1) + \cdots + S_{72}(S_{72}+1)\right) \quad (2)$$



Scheme 1

where all S_i = 1/2, $S_{ij} = S_i + S_j$, $S_i + S_j - 1$, …, $|S_i - S_j|$, here S_{ij} = 1 or 0. Fitting of the magnetic susceptibility data in the 2–30 K range by solving the exchange matrix on the above expression gives: J_{intra} = 10.4 cm^{-1}, J_{inter} = −0.05 cm^{-1}, g = 5.9, with $R = 1.5 \times 10^{-5}$ $\{R = \sum[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/\sum(\chi_M T)_{obs}{}^2\}$ (inset of Fig. 2; for details see ESI†). It should be noted that the above calculation and fit by considering J and g as isotropic are quite rough because the two factors are often anisotropic. A more involved analysis is needed.

The fast-saturated variation on the isothermal magnetization (M) *vs.* the applied field (H) at 2 K and the saturation value of 18.8 $N\beta$ at 50 kOe further confirm the overall intracluster F coupling, and suggest a ground state of S_T' = 7/2 with g = 5.4 (each S_{Co}' = 1/2, Fig. S1, ESI†). This is also well consistent with another estimation judged from the low-field M–T data at 20 Oe, where the maximum of the $\chi_M T$ value (65.8 cm^3 mol^{-1} K) corresponds to S_T' = 7/2 and g = 5.78 (inset of Fig. 2).

One of the characteristics of a SMM, significant anisotropy, was confirmed by the field dependent magnetizations (20–50 kOe) at temperatures in the range 2–20 K, where the isofield lines are far from superposition (Fig. S2, ESI†). However, our effort to extract reliable zero-field splitting (ZFS) parameters of D (axial) and E (rhombic) by ANISOFIT[3a] was hampered by the large orbital-contribution of distorted Co(II) ions.

Another evidence for the possible SMM behavior of **1** is the observation of strong (comparable to the in-phase values) and significantly frequency-dependent out-of-phase ac signals (χ_m'') below 6 K in zero applied dc field, although no maximum was observed down to 1.8 K (Fig. 3). It was noticed that the energy gap (Δ), which is well known to be relevant to the relaxation time (τ_0) in a SMM, can be tuned by an applied field,[1] and so we measured the ac susceptibilities at different dc fields (1 and 3 kOe). As a result, both in-phase and out-of-phase signals moved to higher temperature with increasing the dc field, and most of peaks of χ_{ac}' appeared (Fig. 3 and S3, ESI†). In addition, the absence of the second harmonics at both zero-field and 1 kOe excluded any possibility of 3D order or a spin glass behavior (Fig. S4, ESI†).[13]

The above results suggested that **1** might be a SMM. To further probe the possible SMM behavior, single-crystal hysteresis loops were performed on a micro-SQUID setup (Fig. 4 and S5, ESI†).

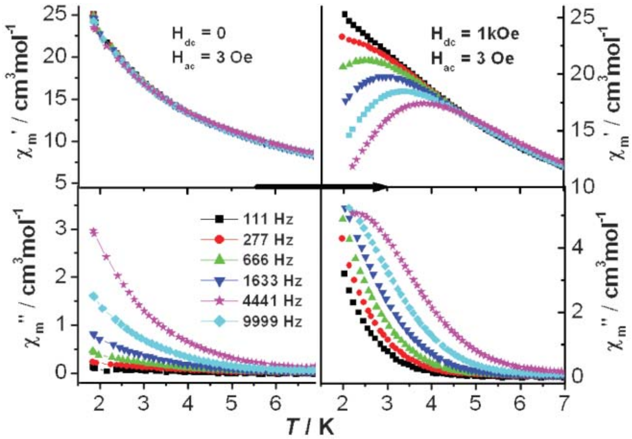


Fig. 3 Temperature dependence of the real (top) and imaginary (bottom) components of the ac susceptibility in zero applied static field (left) and 1 kOe (right) with an oscillating field of 3 Oe.

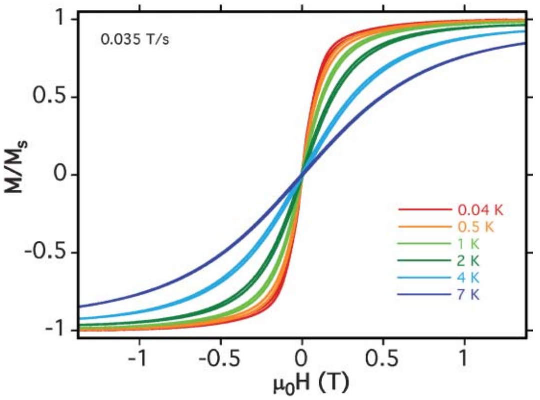


Fig. 4 Single crystal magnetization (*M*) *vs.* field (*H*) hysteresis loops for **1** at the indicated field sweep rates and temperatures.

By using the transverse field method described before,[14] we observed two easy axis directions and clear indication of a negative *D* value, consistent with the slow relaxation as shown in Fig. 3. Unfortunately, only a small degree of hysteresis was observed, which is likely to be influenced by the phonon-bottleneck effect[15] and/or small intercluster AF interactions (Fig. S5, ESI†). It is noted that the hysteresis loops for reported Co(II)-based SMMs seem to be much smaller than those of Mn(III)-based SMMs. One of the reasons might be the significant spin–orbit interactions of Co(II) ions, which not only make it hard for theoretical analysis, but also mix the energy states and thus allow fast quantum tunneling and direct relaxation processes between levels of opposite magnetization. Another reason is presumed to be the effect of the rhombic ZFS parameter (*E*). As Co(II) is a hard-axis ion with positive single-ion ZFS and large *E*-term,[7a] it is obviously hard to satisfy a negative axial ZFS (*D*) as well as a negligible *E*-term resulting from the tensor projection of the single-ion contributions. In this respect, structural anisotropy might be much more important for a Co(II)-SMM system and it would be expected for constructing a real Co(II)-based SMM by adjusting the structural anisotropy. However, it is demonstrated that a planar structure might be not beneficial for resulting in a global easy-axis in this context. In fact, this supposition has also been found in a similar $[Fe^{III}Fe^{II}_6]$ planar compound which exhibited a positive *D* value.[9b] Compared with the previous Co(II)-clusters, **1** has a larger spin ground state due to overall F coupling through EO-azido/methoxy bridges and a planar core structure with $D < 0$. However, this work suggests that a large S_T and negative *D* value are still not sufficient or definitive for a Co(II)-based SMM. More Co(II)-based clusters should thus be investigated for further aspects for this goal.

In conclusion, we have obtained a novel disc-like heptanuclear Co(II)-azido based cluster. The overall intramolecular F coupling resulted in a large ground state and slow relaxation at static zero and non-zero fields, suggesting that **1** is tending towards SMM behavior. It is expected that the ferromagnetic contribution by EO-azide may lead to a new family of SMMs. Investigations on the influence of structural anisotropy on the Co(II)-system, such as some linear Co(II)-clusters, are in progress.

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Notes and references

‡ A methanol solution (10 mL) of NaN_3 (0.6 mmol, 40 mg) and bzp (0.5 mmol) was added dropwise to a stirred methanol solution (10 mL) of $Co(ClO_4)_2 \cdot 6H_2O$ (0.5 mmol, 180 mg). The clear deep-red solution was left at room temperature for several days. Red-plate single crystals were formed. Yield: 52 mg, 35%. Anal. Calc. for **1**, $Co_7C_{75}H_{67}N_{33}O_{19}Cl_2$: C, 40.61; H, 3.04; N, 20.84. Found: C, 40.82; H, 3.07; N, 21.52%. IR (cm^{-1}): 2072vs for stretching of azide; 1100 for ν_{ClO} of ClO_4^-, 3300–3700 (broad) for ν_{OH} of water and methanol molecules.

CAUTION: Although not encountered in our experiments, azide salts are potentially explosive.

§ *Crystal data*: $C_{75}H_{67}Co_7N_{33}O_{19}Cl_2$, M_r = 2218.03, monoclinic, *C*2/*c*, *a* = 26.9497(5), *b* = 17.9499(5), *c* = 23.6303(5) Å, *β* = 121.7376(17)°, *V* = 9721.7(4) Å^3, *Z* = 4, *F*(000) = 4492, GOF = 1.025. A total of 68 171 reflections were collected and 8551 are unique (R_{int} = 0.1367). *R*1 and *wR*2 are 0.0539 and 0.1463, respectively, for 664 parameters and 4768 reflections $[I > 2\sigma(I)]$. The data were collected on a Nonius Kappa CCD with Mo-Kα radiation (*λ* = 0.71073 Å) at 293 K. CCDC 604138. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605459e

¶ The magnetic properties of **1** were performed on a Quantum Design MPMS XL-5 SQUID system and OXFORD Maglab^{2000} system.

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