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# Journal Name

## COMMUNICATION

# An unusual water-bridged homospin Co$^{II}$ single-chain magnet

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**An unusual water-bridged homospin Co$^{II}$ coordination polymer has been successfully assembled, which exhibits slow relaxation of the magnetization at low temperature.**

The development of new molecular nanomagnets has attracted great attention because of their potentials in the fields of high-density storage devices, molecular elelctronics and so on.[1] In particular, single-chain magnet (SCM) is one of such molecular nanomagnets, in which the combination of significant uniaxial anisotropy of spin carriers and large intrachain magnetic interaction between spin carriers leads to high energy barrier for slow relaxation of the magnetization.[2]

The bridging ligand is one of the key factors that can influence the SCM behaviour due to the critical prerequisites of large intrachain magnetic interaction. Different bridging ligands can transmit ferromagnetic (FO), ferrimagnetic (FI) or weak ferromagnetic (WF) interactions with different strengths, depending on the different position of the neighbouring magnetic orbitals.[3] Our group and others have shown that organic radical,[4] azido,[5] carboxylate,[6] phosphate/phosphinate,[7] and oxygen atom[8] can serve as bridging ligands to construct SCMs. Among different bridges, single-atom bridges are good candidates to transmit exchange interactions to show SCM behaviour, because single-atom bridges can not only magnetically couple the neighbouring spins efficiently,[3b] but also help to construct spin canting structures.[9] In the reported single-atom bridges, oxygen atom, especially the carboxylate oxygen, is the most frequent ligand to construct molecule-based weak ferromagnets.[3b,9] Nevertheless, the use of water molecule as bridge is rather rare. Few previous works on the study of magnetic properties of the complexes using water molecule as bridges were always accompanied with other bridges such as carboxylate.[10]

Furthermore, metal ions with highly magnetic anisotropy are favourite to be involved in the construction of SCMs, such as Mn$^{3+}$, Co$^{2+}$, and lanthanide ions.[11] Among these well-studied metal ions, the high-spin Co$^{II}$ ion is one of the best candidates to construct molecular nanomagnets due to its strong magnetic anisotropy.[12] However, Co$^{II}$-based SCMs assembled in high-dimensional networks are still underexplored.[13] As a follow of our study in construction of SCMs by various bridging ligands, a novel three-dimensional (3D) coordination polymer, **NKUMOM-3**, was synthesized via the self-assembly of a custom-designed H$_2$L ligand (H$_2$L = 3,3'-(1,3,6,8-tetraoxobenzol[lmn][3,8]phenanthroline-2,7(1H,3H,6H,8H)diyl)-di-benzoic acid) and CoCl$_2$ salts. **NKUMOM-3** consists of well-isolated metal-oxygen chains and exemplifies a weak ferromagnetic (WF) approach to show SCM behaviours.
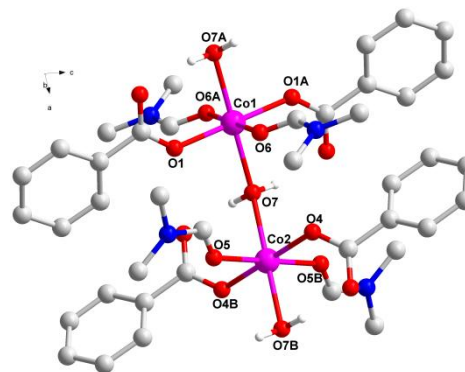


**Fig. 1** The coordination environment of the Co$^{II}$ ions (C gray, Co purple, O red, N blue, H white). Symmetry code: A: -x, 2-y 2-z; B: 1-x, 2-y, 2-z (hydrogen atoms and parts of the ligands are omitted for clarity).

Hydrothermal reaction of CoCl$_2$·6H$_2$O and H$_2$L with a molar ratio of 1 : 1 in a mixed DMF/water solvent at 80 °C for 3 days affords a crystalline coordination polymer, **NKUMOM-3**, with a formula of [Co$_2$(L)$_2$(H$_2$O)$_2$(DMF)$_4$]$_n$. Powder X-ray diffraction (PXRD) measurement supports its stability in air atmosphere and high phase purity (Fig. S3, ESI†). **NKUMOM-3** crystallizes in triclinic space group $P\bar{1}$. There are two crystallographic independent Co$^{II}$ ions (Co1 and Co2, Fig. 1). Co1 and Co2 adopt similar coordination modes, which are in a slightly compressed octahedral geometry, finished by two O atoms from the carboxyl group of the L$^{2-}$ ligand, two O atoms from two DMF molecules and two O atoms from two $\mu_2$-water bridges. Neighbouring Co$^{II}$ ions are linked by $\mu_2$-water bridges with Co-O (H$_2$O) distances of 2.233(3) and 2.250(3) Å. Those water bridges are indicated by the Co-O (H$_2$O) distances (2.223(2) and 2.304(2) Å), whereas Co-O (OH) or Co-O (O$^{2-}$) bond lengths are around 1.9 and 1.8 Å, respectively.[14] The distance of the

neighbouring $Co^{II}$ ions connected by water bridge is 4.199(5) Å (Table S2, ESI†). There is only one binding mode of the ligand $L^{2-}$ in this coordination polymer. Every deprotonated carboxylate group coordinates with one $Co^{II}$ ion by a monodentate coordination mode. $Co^{II}$ ions are connected via the $\mu_2$-water bridge to form infinite one-dimensional (1D) chains, which are further connected by $L^{2-}$ to form a 3D network (Fig. 2). It is noted that the networks are two-fold interpenetrating. The shortest distance of the $Co^{II}$ chains is 10.432(11) Å (Fig. S4, ESI†).
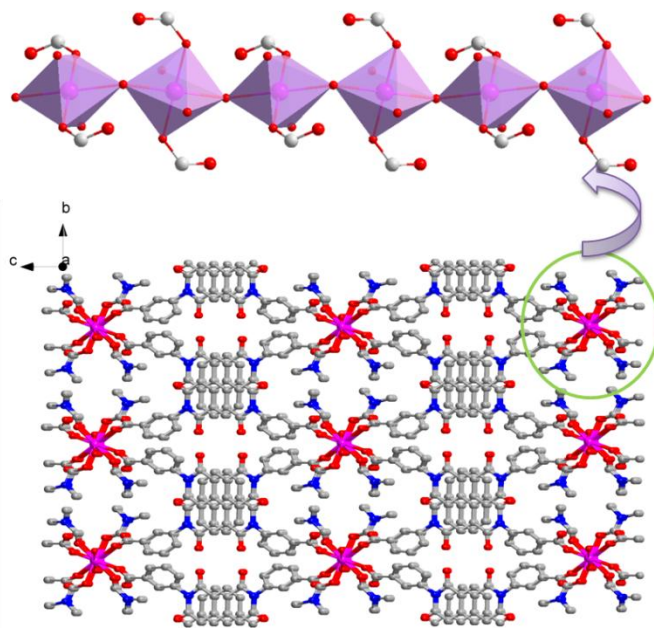


**Fig. 2** Perspective views of the one-dimensional water bridged chain with the $Co^{II}$ atoms highlighted as purple polyhedral (top), and three-dimensional network (bottom) (C gray, Co purple, O red, N blue).

The dc magnetic susceptibilities were measured in the temperature range of 2-300 K under an applied magnetic field of 1 kOe (Fig. 3a). At room temperature, $\chi_M T$ is 6.63 $cm^3\,mol^{-1}$ K, which is higher than the value expected for two $Co^{II}$ ions (3.74 $cm^3\,mol^{-1}$ K), due to the spin-orbit coupling. $\chi_M T$ firstly decreases on lowering the temperature to a minimum of 2.02 $cm^3\,mol^{-1}$ K at 11 K. This behaviour is attributed to the spin–orbit coupling and possible antiferromagnetic effects.[8] Below 11 K, $\chi_M T$ increases abruptly to a maximum of 3.93 $cm^3\,mol^{-1}$ K at 3.7 K, and then decreases rapidly upon further cooling. The data above 80 K can be well fitted by Fisher 1D chain model (Fig. S5, ESI†),[15] to give $J$ = -23.09 $cm^{-1}$, $g$ = 2.86, $R = 1.88 \times 10^{-5}$ ($R = \Sigma[(\chi_m T)_{obs}-(\chi_m T)_{calcd}]^2/\Sigma[(\chi_m T)_{obs}]^2$). The value of the $g$ factor is well in the range of reported $Co^{II}$ SCM.[13a] The $M$ vs $H$ curve (Fig. S6, ESI†) shows that the magnetization first increases steeply at the initial low field, and then increases slowly to 1.92 Nβ at 70 kOe without achieving saturation, due to the anisotropy of $Co^{II}$ ion in **NKUMOM-3**. Field-cooled magnetizations (FCM) and zero-field-cooled magnetizations (ZFCM) are almost identical (Fig. S7, ESI†), which is consistent with no observation of a clear hysteresis loop at 2 K (Fig. S8, ESI†).

Ac susceptibility studies were performed under zero dc fields in order to further understand intrinsic magnetic properties of the 1D $\mu_2$-water bridged $Co^{II}$ chain. Both the in-phase ($\chi'$) and out-of phase ($\chi''$) susceptibility curves show peaks at low temperatures and obvious frequency dependence (Fig. S9, Fig. S10a, ESI† and Fig. 3b). The frequency shift parameter $\varphi$ is 0.19 ($\varphi = (\Delta T_p/T_p)/\Delta(\log v)$),

excluding the possibility of spin-glass behaviour and lies well in the range (0.1 < $\varphi$ < 0.3) for superparamagnetic behaviour.[16] The relaxa-
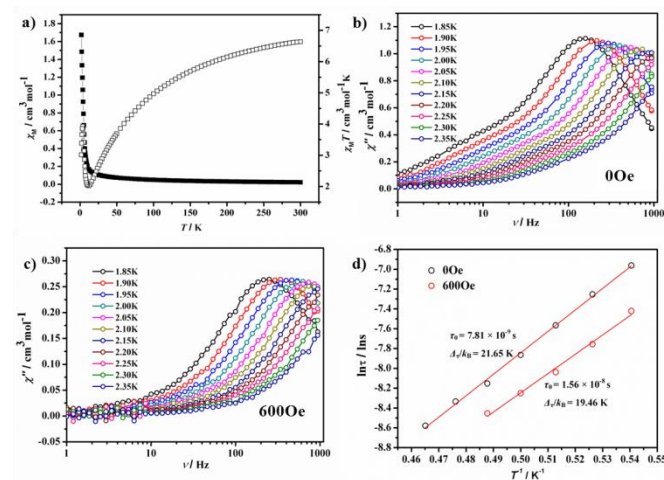


**Fig. 3** a) Temperature dependence of $\chi_M T$ (□) and $\chi_M$ (■) at 1000 Oe. b) Frequency dependence of out-of-phase ($\chi''$) ac susceptibilities measured on a polycrystalline sample in zero dc field. Solid lines are eye guides. c) Temperature dependence of $\chi''$ measured on a polycrystalline sample in 600Oe dc field. Solid lines are eye guides. d) ln($\tau$) verse $T^{-1}$ at 0 Oe and 600 Oe dc fields, respectively. The red lines are the best fits.

tion time derived from the $\chi''$ peaks follow the Arrhenius law of $\tau = \tau_0\exp(\Delta\tau/k_B T)$, with $\tau_0 = 7.81 \times 10^{-9}$ s and $\Delta_\tau/k_B$ = 21.65 K, suggesting a thermally activated relaxation (Fig. 3d). The $\tau_0$ and $\Delta_\tau/k_B$ values lie in the usual range of SCMs.[3c] The Cole-Cole diagram was fitted separately by a generalized Debye model,[17] considering two relaxation processes (A and B) to result in αA and αB covering the ranges of 0.12 (1.85 K)-0.20 (2.25 K) and 0.34 (1.85 K)-0.25 (2.25 K), respectively (Fig. S11a and Table S3, ESI†).[18] To further investigate the slow relaxation, ac susceptibilities were measured under different dc fields (Fig. S12, ESI†). From the Cole-Cole plots in different dc fields, the two relaxation processes change to single relaxation process at 600 Oe, which was also confirmed by the fitting using the generalized Debye model (Table S4, ESI†). This is indicative of the compensation of the external dc field and the interchain interaction. Ac susceptibilities were further studied under 600 Oe dc field. Both the $\chi'$ and $\chi''$ are strongly frequency dependent at low temperatures (Fig. S10b, ESI† and Fig. 3c). The relaxation time following Arrhenius law gives $\tau_0 = 1.56 \times 10^{-8}$ s and $\Delta_\tau/k_B$ = 19.46 K (Fig. 3d). Moreover, the Cole-Cole plots are well described by the modified Debye function (Fig. S11b, ESI†, Table S3, ESI†). The best fitting results of $\alpha$ values are less than 0.22, suggesting single magnetic relaxation process under dc field larger than 600 Oe.

A further analysis of the plots of ln($\chi T$) vs. 1/T with different dc fields for the 1D behaviour was performed (Fig. 4). By fitting the linear regime data (4-8 K) with the equation of $\chi T = C_{eff}\exp(\Delta_\xi/k_B T)$, $\Delta_\xi/k_B$, of 6.44 K (with $C_{eff}$ = 1.04 $cm^3mol^{-1}$K), was obtained. The linearly increasing of ln($\chi T$) vs. 1/T also supports the uniaxial anisotropy of the Ising-like chain in the coordination polymer.[8] Upon lowing the temperature, ln($\chi T$) at zero dc field goes to the saturation of 1.87 $cm^3\,mol^{-1}$ K, well confirming the SCM-like behaviour.[2a]

Nowadays, limited SCMs using $Co^{II}$ as spin carrier are reported. Interchain magnetic interaction may lead to the antiferromagnetic ordering of the SCM chain.[19] The results from our group and others have also proofed such assertion experimentally.[4b,8,20] To avoid such ordering, a combination of short bridging ligands to transmit strong intrachain magnetic interaction and long bridging ligand to magnetically separate the chain effectively is a promising route. In

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addition, linking the SCM chains into higher dimensional framework via covalent coordination bonds may construct more robust materials, better for potential applications. This work shows a rare example that SCM behavior still survives when the magnetic chains were assembled into the framework structure, without the occurrence of long-range ordering.
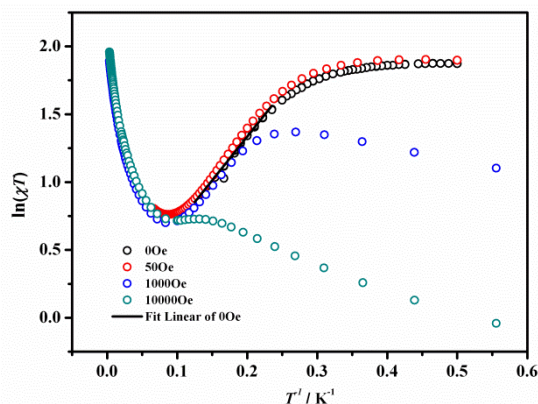


**Fig. 4** The $\ln(\chi T)$ versus $1/T$ of **NKUMOM-3** at different external field. The solid line is the fitting result of the data measured at 1 Hz frequency, 3 Oe oscillating field and zero external field.

In summary, a 3D cobalt coordination polymer has been constructed by linking water-bridged cobalt chains via a long linker of dicarboxylic ligand to show interesting SCM behaviour. This work illustrates an unusual example of SCM assembled in a framework with three-dimensional structure, which could be suggested as a framework approach. More works to explore new molecular magnetic materials via this approach are currently underway in our laboratory.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, EA, IR, TGA, PXRD, and magnetic properties. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/.

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