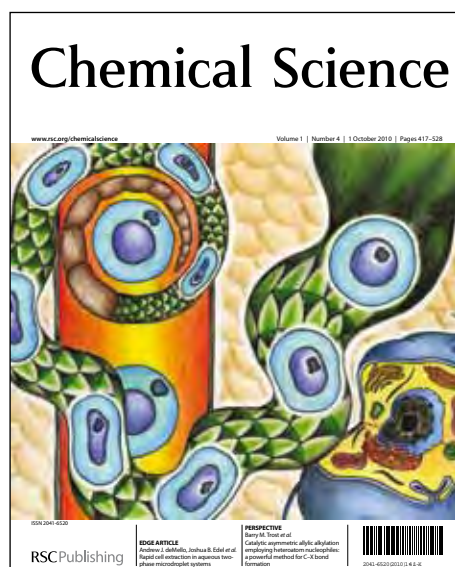


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EDGE ARTICLE

Zero-Field Slow Magnetic Relaxation from Single Co(II) Ion: A Transition Metal Single-Molecule Magnet with High Anisotropy Barrier

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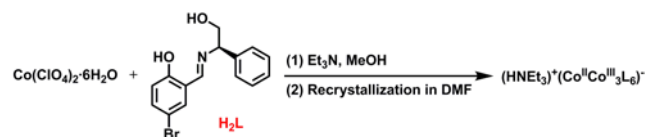
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An air-stable star-shaped $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_3$ complex with only one paramagnetic Co(II) ion in the D_3 coordination environment has been synthesized from chiral Schiff base ligand. Magnetic studies revealed that this complex exhibited slow magnetic relaxation in the absence of applied dc field, which is one of the main characteristics of Single-Molecule Magnet (SMM). The relaxation barrier is as high as 109 K, which is quite large among the transition-metal ion-based SMMs. The complex represents the first example of zero-field SMM behavior in a mononuclear six oxygen-coordinate Co(II) complex.

Introduction

Single-molecule magnets (SMMs) provide wonderful models for understanding the quantum phenomenon in mesoscopic world and have potential applications in information storage and quantum computing and thus have invoked wide interests in chemical, physical and material sciences.^{1,2} Since the first Single-molecule magnets (SMMs) Mn_{12}OAc was discovered in 1990s,³ various cluster-type molecules with slow magnetic relaxation at low temperature, including transition-metal clusters, 3d-4f polynuclear compounds, lanthanide clusters, and radical containing systems,⁴ have been reported. In 2003, Ishikawa et al observed the slow magnetic relaxation in single-ion magnet (SIM) $\text{Tb}(\text{III})\text{Pc}_2$ which contains a single paramagnetic Tb^{3+} ion.⁵ Since then, several SIMs containing single lanthanide or actinide ion have also been reported.⁶ These mono rare-earth-based SMMs are structurally simple, with the relaxation barrier reaching as high as 300 K. However, it is still a challenge to design SIMs displaying slow magnetic relaxation from single transition-metal-ion complexes. Previously, Gao et al reported that the field-induced slow magnetic relaxation could occur in coordination polymers containing magnetically isolated Nd(III), Gd(III), and transition metal ions Fe(III), Cu(II), and Mn(II) ions.^{7,8} Different from the simple Mn(II) and Cu(II) ions, which are magnetically isotropic, several mononuclear Fe(II) and Co(II) complexes could exhibit slow magnetic relaxation under nonzero dc field due to single-ion anisotropy.⁹ Long et al found that tetrahedral coordinated Co(II) complex $(\text{Ph}_4\text{P})_2^+[\text{Co}(\text{SPh})_4]^{2-}$ showed slow magnetic relaxation under zero dc field with an anisotropy barrier of 30 K.¹⁰ Mossin et al reported that five coordinated Fe(III) complex $(\text{PNP})\text{FeCl}_2$ ($\text{PNP} = \text{N}[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$) also exhibited magnetic relaxation under zero dc field with an energy barrier of 47 K.¹¹ More recently, Long et al further developed a series of two-coordinate Fe(II) mononuclear complexes that could behave as SMMs and possess an anisotropy barrier as high as 261 K.¹² It

is expected that SMMs containing one transition-metal ion will provide simpler models for studying their spin dynamics. However, unlike the lanthanide SIMs, the examples of transition-metal-based SIMs which display high relaxation barrier are still limited. Herein, we report a chiral star-shaped $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_3$ compound $(\text{HNEt}_3)^+(\text{Co}^{\text{II}}\text{Co}^{\text{III}}_3\text{L}_6)^-$ (**1**) which exhibits slow magnetic relaxation with a high anisotropy barrier of 109 K in the absence of an applied dc field. To the best of our knowledge, this complex represents the first example of the zero-field SMM behavior displayed by a mononuclear six oxygen-coordinate transition metal complex.



Scheme 1

Results and discussion

The air-stable complex **1** with the formula $(\text{HNEt}_3)^+(\text{Co}^{\text{II}}\text{Co}^{\text{III}}_3\text{L}_6)^-$ was obtained as dark red crystals from the reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with salicylaldehyde Schiff base ligand H_2L (Scheme 1, $\text{H}_2\text{L} = R\text{-4-bromo-2-}((2\text{-hydroxy-1-phenylethyl)imino)methyl)phenol$. see SI for synthetic details). X-ray single-crystal structure analysis revealed that **1** crystallizes in the chiral space group $P2_12_12_1$. The complex is reminiscent of Hexol,¹³ which represents the first noncarbon-containing chiral compound. The four cobalt ions in the tetra-nuclear core formed a nearly centered equilateral triangle with the length of the three sides being 5.41, 5.48, and 5.51 Å, respectively. The detailed data of the bond length and angle are listed in Table S1. The three peripheral Co(III) ions are located in a slightly distorted octahedral ligand field and diamagnetic in character. The central Co(II) ion is coordinated with six oxygen atoms, which gave rise to a slightly distorted triangular prism of D_3 symmetry with

Co1...O distances ranging from 2.09 Å to 2.17 Å (Fig. 1b, 1c). The oxidation states of the four Co ions were confirmed by bond length consideration, charge balance, and BVS calculations (For BVS calculation result, See Table S2). The single-crystal structure revealed that the negative charge of the (Co^{II}Co^{III}₃L₆)⁻ skeleton is compensated by one protonated triethylamine. ESI-MS and IR spectra can also provide some cross evidence to support the structure of negative cluster. These results are helpful to the oxidation state determination of Co ions (for the ESI-MS spectrum see Figure S1). In the crystal structure, the paramagnetic Co(II) ions are well magnetically isolated from each other by three peripheral diamagnetic Co(III) ions, the Schiff base ligand, counter cation, and DMF solvents. The shortest distance between the Co(II) ions of neighboring clusters is 12.66 Å (Fig. S2).

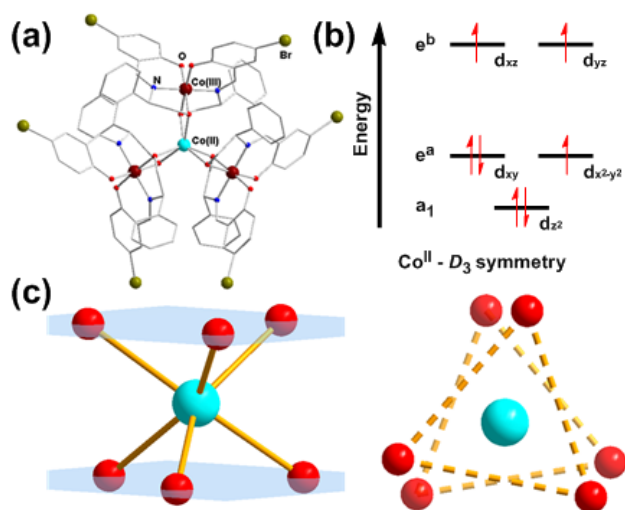


Fig. 1 (a) The molecular structure of **1** (Counter cation of (HNEt₃)⁺ and hydrogen atoms have been omitted for clarity). (b) The simplified d⁷ electron configuration for the central Co(II) ion with D₃ symmetry. (c) The coordination model of central Co(II) ion.

Magnetic measurements were performed on polycrystalline samples of **1** using Quantum-Design MPMS and PPMS magnetometers. It was found that the temperature dependence of its molar magnetic susceptibility is characteristic of the non-interacting mononuclear Co(II) complexes. The corresponding $\chi_M T$ vs. T plot is provided in Figure 2. The $\chi_M T$ value at 300 K is 3.39 cm³ K mol⁻¹, which is in the range of a single non-interacting d⁷ Co(II) ion with the considerable contribution of the orbital angular momentum. It remains roughly constant at high temperature range, then decreasing slightly due to zero field splitting of the Co(II) ion. The magnetization was measured up to 12 T dc field at 2, 4, 8, 12, and 17 K, respectively. The non-superposition of the M vs. H/T plots at higher field (Inset, Figure 2) implies the presence of significant magnetic anisotropy. A spin Hamiltonian of equation (1) is utilized to describe the magnetic anisotropy qualitatively although it is not very sensitive to the change of large D value in compound **1**:

$$\mathbf{H} = DS_z^2 + E(S_x^2 + S_y^2) + g_{\text{iso}} \mu_B \mathbf{S} \cdot \mathbf{B} \quad (1)$$

where μ_B is the Bohr magneton and D , E , S , \mathbf{B} represent the axial and rhombic zero-field splitting (ZFS) parameters, the spin, and magnetic field vectors, respectively. The magnetization data at low temperature of 2, 4, and 8 K were fitted using the ANISOFIT

2.0 program (Fig. S4),¹⁴ which take account of the phenomenological spin Hamiltonian above. The obtained D value was -115 cm⁻¹, with the corresponding E and g being 2.8 cm⁻¹ and 3.05, respectively. The large negative D value indicated that **1** has a large uniaxial anisotropy.

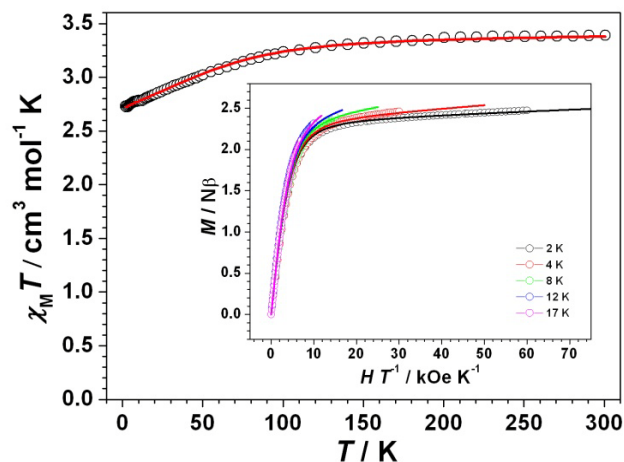


Fig. 2 Temperature dependence of $\chi_M T$ under 1 kOe applied dc field at 2–300 K for the polycrystalline sample of **1**. (The red solid line represents the best simulation of magnetic susceptibilities based on ligand field theory). Inset: Experimental and theoretical M vs. H/T plots at different temperatures (2 K, 4 K, 8 K, 12 K, and 17 K) of **1**. The symbolized points are experimentally measured value under magnetic fields up to 12 T and the solid lines are theoretical curve under magnetic fields up to 20 T calculated with CASSCF/CASPT2 method.

In order to probe the magnetic dynamic behavior, the ac susceptibilities of **1** at various frequencies in the absence of dc field were also measured at low temperature (see Fig. 3 and Fig. S5). Both in-phase (χ') and out-of-phase (χ'') susceptibilities showed significant frequency dependence within a broad temperature range. The χ'' peaks from $\nu = 100$ Hz to $\nu = 10000$ Hz appeared in the higher temperature range of 9 K to 22 K and upturned strongly below 9 K. The relaxation energy barrier U_{eff} , fitted by Arrhenius law from the high temperature regime of the relaxation, equaled 109 K.

The upturn of χ'' curve at low frequencies and low temperature range could be attributed to the impact of the quantum tunneling of the magnetization (QTM) on the thermal-assisted process like the situation in lanthanide, actinide, and other 3d metal based SIMs. In order to reduce the QTM effect, ac measurements under the applied dc field of 1500 Oe were performed at various frequencies and temperatures, respectively. The almost disappearance of the upturns of χ'' indicated QTM was reduced dramatically (Fig. S7). Arrhenius analysis on the χ'' peaks under 1500 Oe dc field indicated U_{eff} was increased to 124 K, which was only slightly higher than that under the zero dc field (Fig. S8). The χ'' vs. ν curves in the low temperature range in the absence or under an applied dc field of 1500 Oe both displayed significant frequency dependence and gave similar energy barrier values (Fig. S9-S16). The χ'' vs. χ' data at different temperatures in the absence of a dc field, fitted by the Debye Model,^{15,16} definitely suggested the presence of a single relaxation process in the measured temperature range (Fig. S12). Due to the influence of QTM, magnetization hysteresis, another important character of magnetic bistability of SMM, was not observed in MPMS

measurement at 1.8 K (Fig. S18). However, a very small bifurcation can be observed when the measured temperature down to 0.6 K (Fig. S19).

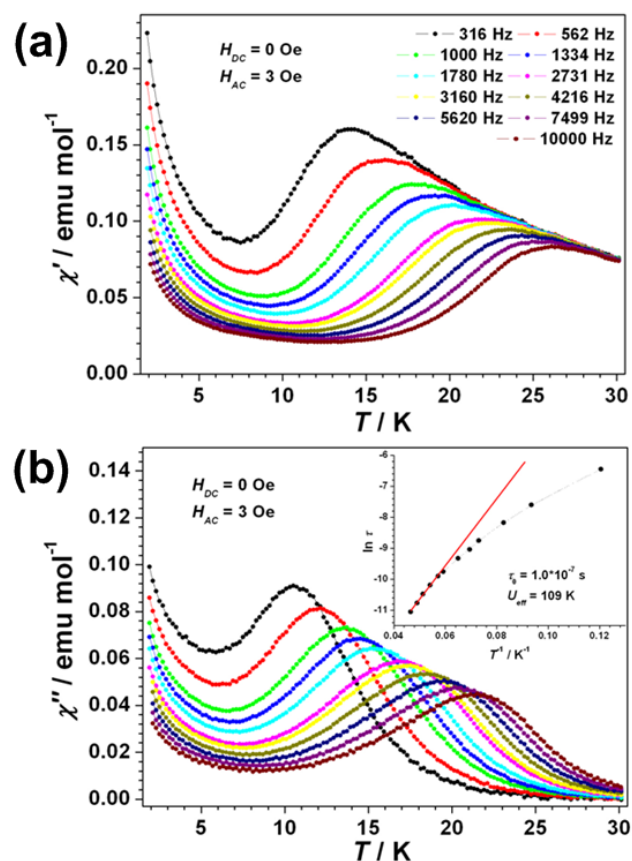


Fig. 3 Temperature dependence of (a) χ'_M and (b) χ''_M of **1** at various frequencies in the absence of dc field. Inset, Arrhenius analysis of the relaxation processes.

In order to understand the magnetic anisotropy and slow magnetic relaxation of **1**, theoretical studies were further performed using both the effective Hamiltonian and *ab initio* methods. The effective Hamiltonian of equation (2) was used to include the ligand field effect and spin-orbit coupling simultaneously:

$$\hat{H} = \hat{H}_0 + \hat{H}_{ee} + \hat{H}_{SO} + \hat{H}_{LF} + \hat{H}_{MF} \quad (2)$$

where \hat{H}_0 , \hat{H}_{ee} , \hat{H}_{SO} , \hat{H}_{LF} , \hat{H}_{MF} account for the Hamiltonians of zero-level term, interelectronic repulsion, spin-orbit effect, ligand field effect, and Zeeman effect, respectively. All the possible 120 microstates for the electronic configuration $3d^7$ of Co(II) have been adopted as basis sets to calculate the energy spectrum and simulate the corresponding magnetic properties. The magnetic susceptibility data were fitted well from 2 K to 300 K with the Hamiltonian above in a D_3 symmetry using the program CONDON developed by Lueken and co-workers (Fig. 2).¹⁷ Generally, for the isolated high spin Co(II) ion, the ground state term F^4 is well separated with excited P^4 and G^2 state. The magnetic properties at low temperature are mainly determined by ground state and its fine structure. The D_3 ligand field of complex **1** is a subgroup of O_h point group. The 28-fold degenerated 4F ground state of free Co(II) ion is firstly split into $^4T_{1g}$ ground state, a first $^4T_{2g}$ and a second $^4A_{2g}$ excited state (Tanabe-Sugano

diagram) in an octahedral ligand field. When further lowered the symmetry by a trigonal distortion to D_3 , the 12-fold degenerated ground $^4T_{1g}$ state is split into a 4E (8-fold degenerate) and a 4A_2 (4-degenerate) state. Taking the spin-orbit coupling into account, the ground 4E state is split further to four pairs of Kramers doublets.¹⁸ If the ground state energy was taken as the origin, the relative energies of these four pairs fitted from magnetic susceptibility data are 0.0, 201.4, 879.6, and 960.8 cm^{-1} , respectively.

The ground state wavefunction is mainly composed of microstates with $M_J = \pm 9/2$ and $\pm 3/2$ and mixed by the small contribution of microstates with $M_J = \pm 7/2$ and $\pm 1/2$. The main part of the first excited state wavefunction is changed to microstates with $M_J = \pm 7/2$ and $\pm 1/2$ besides the small component of $M_J = \pm 5/2$ states. The same components contained in the ground and first excited states increase the possibility of QTM and could reduce the effective barrier of thermal activated magnetic relaxation. So the energy gap of 291 K (201.4 cm^{-1}) between the ground and first excited state is much higher than the observed relaxation barrier of 109 K obtained from the Arrhenius fitting. The fitted non-negligible rhombic ZFS parameter E of 2.8 cm^{-1} from measured magnetization data also indicated that the ground eigenstate should be the superposition of different M_J states.

Complete-active-space self-consistent-field (CASSCF), second order perturbation (CASPT2) and followed RASSI calculations were also performed to extract the electronic structure information of **1**. Again, taking the ground state energy as origin, the energy levels of the lowest four Kramers doublets are 0.0, 216.4, 819.1, and 1122.0 cm^{-1} , respectively. This energy spectrum of low-lying excited state is consistent with the results from spin-Hamiltonian approach. The computed magnetic susceptibilities and magnetization were well consistent with the experimental measurements (see SI for computation details and plots in Figure 2), indicating that the calculated energy spectrum could well produce the magnetic properties according to the Boltzmann distribution of spin electrons.

The calculated zero-field-splitting parameter D with CASSCF/RASSI method was -107 cm^{-1} , which indicated large uniaxial anisotropy of **1**.¹⁹ The calculated g factors also confirmed the easy-axis anisotropy of **1** with $g_z = 7.57$, $g_y = 0.59$, $g_x = 0.53$. Due to the large D value of **1**, there will be no population of the excited levels in the measured temperatures, the M vs. H/T curves are almost coincided when the magnetic field is smaller than 5 T (Fig. S20). However, upon increasing the magnetic field, the non-superposition of the M vs. H/T plots appears again at the field of 12 T (Inset, Fig. 2) which also confirmed that the ZFS was very large in complex **1**. If complex **1** was assumed to be describe as a giant spin model like cluster-type SMMs, the relaxation barrier from $|D|(S^2 - 1/4)$ should be 299 K, which was also in good agreement with the results obtained from the effective Hamiltonian method and CASSCF based calculations. Comparing with the fitted relaxation barrier of 109 K from Arrhenius law, the energy barrier from both effective Hamiltonian method and CASSCF based calculations was much higher than the expected one. Since the QTM process was not quenched successfully by non-zero dc field (Fig. S6-8) as mentioned above, the heavy QTM seemed to be the possible

reason that the experimentally observed relaxation barrier is lower than the theoretical value. The relatively small quantum number of angular momentum in transition-metal ions also contributed to the strong QTM and maybe another reason why it was difficult to find the hysteresis in the single TM ion based SMMs. When it was calculated with the spin-Hamiltonian approach, the wavefunction of the ground and first excited states both contained the small angular momentum components with $M_J = 3/2$ or $1/2$. The fact that the relaxation barrier is lower than the theoretical expectation was also found in the $\text{Co}(\text{SPh})_4^{2-}$ SMM reported by Long et al.¹⁰ However, the D value of **1** was too large to be determined by the EPR equipment nowadays. Consequently, the single Co(II) ion in **1** is distinguished with large uniaxial anisotropy, which was confirmed by both the magnetic measurements and the theoretical computational studies.

The relaxation barriers of **1** and Long's two-coordinate Fe(II) series complexes are all high compared with the cluster-type SMM or transition metal single-ion magnets.²⁰ In complex **1**, the strong slow magnetic relaxation under zero dc field of Co(II) ion could be attributed to two factors. Firstly, the special coordination environment with the D_3 symmetry and the strong spin-orbit coupling effect of Co(II) ion provide a considerable anisotropy energy. By using the method of symmetry measures developed by S. Alvarez and D. Avnir et al.,²¹ we further analyzed the deviation from the ideal D_3 symmetry of the central Co(II) ion. The calculated deviation to the ideal D_3 symmetry was only 0.045, suggesting the local symmetry of the central Co(II) ion was nearly an ideal D_3 point group. The calculated E/D ratio of 1/40 using the CASSCF/RASSI method also indicated a nearly full uniaxial anisotropy for **1**. The weak transverse magnetic anisotropy reduced the impact of QTM to thermal-assisted relaxation and maintained the high relaxation barrier. Secondly, the three peripheral diamagnetic Co(III) ions naturally reduced the spin density of the large region of the molecule and dramatically weakened the exchange and dipolar interactions between paramagnetic ions in the lattice. This dilution-like effect was observed in several lanthanide-based SIMs whose slow magnetic relaxation were enhanced by non-magnetic Yttrium dilution for the reduction of dipolar-dipolar interactions.^[6a,6d,6f,6g] Recently, Cano et al reported that a six nitrogen-coordinate mononuclear Co(II) complex displayed field-induced single-molecule magnet behavior. However, different from **1**, the field-induced relaxation came from a transverse anisotropy.^{9g}

Conclusions

In summary, an air-stable $\text{Co}^{\text{II}}\text{Co}^{\text{III}}_3$ complex was synthesized from chiral Schiff base ligand. Magnetic studies demonstrate the slow magnetic relaxation in the absence of applied field originated from the individual Co(II) ion in D_3 symmetry. Although it is difficult to utilize single transition metal ions with traditional six-coordinate octahedral field model to construct SMMs because of the strong quench of the orbit contribution, this work shows that with a triangular prism coordination model, single six-coordinated transition metal can form SMM. We believe that this study will deepen and accelerate studies on the SIMs owing to the simple geometry, nearly ideal local axial symmetry, and distinguished magnetic relaxation barrier of the new model. Further investigation and systematic tuning magnetic

anisotropy of this family of complexes and other mononuclear Co(II) complexes with the same local symmetry are under way.

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- [†] Electronic Supplementary Information (ESI) available: Experimental procedure, structure and magnetic characterization, Figures S1-S21, Tables S1-S2, and the cif files of **1**. See DOI: 10.1039/b000000x/
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