A dicobalt(II) single-molecule magnet via a well-designed dual-capping tetrazine radical ligand

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Supporting Information

ABSTRACT: The recent years have witnessed the glory development for the construction of high-performance mononuclear single molecule magnets (SMMs) within a specific coordination geometry, which, however, is not well applied in cluster-based SMMs due to the synthetic challenges. Given that the monocobalt(II) complexes within a trigonal prism (TPR) coordination geometry have been classified as excellent SMMs with huge axial anisotropy (D ≈ –100 cm^-1), here we designed and synthesized a new dual-capping tetrazine ligand, 3,6-bis(6-(di(1H-pyrazol-1-yl)methyl)pyridin-2-yl)-1,2,4,5-tetrazine (bpptz), and prepared a novel dicobalt(II) complex, [Cp2CoIII] [{(hfac)CoII}2(bpptz^-)], where the incorporation of 2d-symmetric cobalt(II) blocks paramagnetic oxamido-Cu(II) bridging unit, in which the Co(II) centers are well pocketed by the bpptz^- radical ligand enwraps two Co(II) centers within quasi-TPR geometries, which are further bridged by the tetrazine radical in trans mode. The magnetic study revealed that the interaction between the Co centers and the tetrazine radical is strongly antiferromagnetic with the coupling constant (J) of –65.8 cm^-1 (in the –2J formalism). Remarkably, 1 exhibited the typical SMM behavior with an effective energy barrier of 69 cm^-1 under a 1.5 kOe dc field, among the largest for polynuclear transition metal SMMs. In addition, DFT and ab initio calculations suggested that the presence of strong Co(II)-radical magnetic interaction effectively quench the QTM effect and enhance the barrier height for the magnetization reversal.

INTRODUCTION

The engineering of single molecule magnets (SMMs) towards high effective energy barrier (Ueff) or enhanced blocking temperature (T8), has received remarkable achievements in recent years.1 The energy barrier for spin reversal is directly coupled with the magnetic anisotropy, which can be fine-tuned via the geometry modulation in mononuclear complexes.2 Representatives can be found in Dy(III)-based complexes within the pentagonal bipyramidal (PBP) geometry or metallocene,1b,2a-c,3 giving the observed magnetic hysteresis within the pentagonal bipyramidal (PBP) geometry or metallocene,1b,2a-c,3 giving the observed magnetic hysteresis above liquid nitrogen temperature and the energy barriers over 1500 cm^-1. On the other hand, a majority of 3d transition metal SMMs within the low-coordinate environment have also been reported to show huge magnetic anisotropy with the barriers up to several hundreds of wavenumbers due to the first- or enhanced second-order spin-orbit coupling (SOC).1a,2d,4

In addition to the geometry modulation of single-ion magnetic anisotropy, incorporation of strong intramolecular magnetic coupling (J) represents another important way to achieve true bistability and longer relaxation time, in which realization of both specific geometry and strong magnetic coupling within one molecule is extremely limited.5 It should be mentioned that if J is not sufficiently large, the relaxation would proceed through the low-lying excited states, leading to an undesirable suppression of the SMM property. In this respect, radical-bridged SMMs are believed more promising, because the exchange coupling through the direct overlap of magnetic orbitals between the metal ions and radical ligands is usually strong.5d,A A good example was given by Sarkar and co-workers where the incorporation of D2h-symmetric cobalt(II) blocks into an exchange-coupled dinuclear system via a radical bridge leads to a 350-fold increase of the magnetization relaxation time.5b Long et al. recently constructed a series of semiquinone radical-bridged dinuclear complexes where the metal centers adopt a trigonal bipyramidal (TPB) geometry.5d

In comparison with the low-coordinate metal complexes, higher coordinate ones within a certain coordination geometry are also capable of exhibiting considerable magnetic anisotropy, and additionally, they are more air- and moisture-stable. Specifically, for the octahedral mononuclear Co(II) complexes,7 the easy-plane magnetic anisotropy arises mainly from dxz and dxy transitions and slow magnetic relaxation is dominated by the Raman process involving both acoustic and optical phonons. Lowering the symmetry for the trigonal antiprism (aTPR) or trigonal prism (TPR) geometry, appreciable axial anisotropy on the order of D ≈ –100 cm^-1 is realized due to the second-order SOC originated from the less degeneracy of the highest double-occupied and lowest single-occupied dxz and dxy orbitals.8 Unfortunately, for the aTPR-Co(II) SMMs, the considerable E-term anisotropy often led to the prevailing QTM at zero field. Alternatively, a series of rigid tripod hexadentate caging ligands (tppm and derivatives, Scheme 1) were explored by us for well pocketing the metal centers into the desired TPR geometry.8b,9 The related works demonstrated that the E-term is negligible in a perfect TPR geometry, which resulted in an impressive barrier of 192 cm^-1 under zero dc field and pronounced hysteresis at below 3 K.9c Furthermore, we prepared a new rigid tetradentate ligand (PyPz3, Scheme 1) by tailoring two-coordinate sites of the tppm derivatives, and constructed a trinuclear [Co-Cu-Co] complex by using a paramagnetic oxamido-Cu(II) bridging unit, in which the Co(II)
centers adopt a distorted TPR geometry, and the Co(II) and Cu(II) ions are antiferromagnetically coupled ($J = -31 \text{ cm}^{-1}$). However, the significant geometry distortion and the non-parallel alignment of the easy axes (quasi-C2 axes) of the two Co(II) centers led to the considerable QTM and a small $\mu$ of 24 cm$^{-1}$.

To address the above questions and further strengthen the intramolecular coupling, we turned our interest in the s-tetrazine bridging ligands, which are known to be readily reduced to free radicals. Especially, the magnetic coupling between the tetrazine radical and metal ion was found either strongly antiferromagnetic ($J_{\text{Co-radical}} \approx -70 \text{ cm}^{-1}$) or ferromagnetic ($J_{\text{Ni-radical}} \approx +100 \text{ cm}^{-1}$). Notwithstanding, only a handful of number of complexes based on s-tetrazine radical bridges were reported, and very few exhibited SMM behaviour, including one of our recent works for a [Co$_4$] square complex. Here, we designed and prepared a new dual-capping s-tetrazine ligand, 3,6-bis{6-(di(1H-pyrazol-1-yl)methyl)-pyridin-2-yl}-1,2,4,5-tetrazine (b pptz, Scheme 1), with which a dicobalt(II) complex, [Co$_3$(b pptz)][(hfac)Co$_2$]2·2Et$_2$O (1), was constructed. As expected, the Co(II) centres are caged and restricted within the quasi-TPR geometries, and ligated by one b pptz$^-$ radical ligand in trans-mode. Remarkably, magnetic and theoretical studies revealed the strong metal-radical coupling ($J_{\text{Co-radical}} = -65.8 \text{ cm}^{-1}$) and the appreciable uniaxial magnetic anisotropy ($D_{\text{Co}} = -49.6 \text{ cm}^{-1}$) engendered by the TPR coordination environment, leading to the typical SMM behaviour with an effective energy barrier of 69 cm$^{-1}$, among the largest for polynuclear transition metal SMMs.

**EXPERIMENTAL SECTION**

**Materials and Physical Measurements.** The 6-(di(1H-pyrazol-1-yl)methyl)pyridinonitrile [HC(Pz)2(3-CNPy)] was synthesized based on the previous literature. All other chemicals and reagents were commercially available and used as received. The syntheses were carried out under an Argon atmosphere using a glove box.

**Synthesis of b pptz.** An ethanol solution (20 mL) containing [HC(Pz)$_2$(3-CNPy)] (4.0 mmol, 1.0 g), NaH/NH$_3$/H$_2$O (12.0 mmol, 0.61 g) and $S_8$ (0.40 mmol, 0.013 g) was stirred overnight at 90 °C. After cooling to RT, the mixture was filtered, and the residue was collected and washed with water and EtOH. The solid was then suspended in HAC (10 mL), to which NaNO$_2$ (8.0 mmol, 0.7 g) and NaN$_2$O (8.0 mmol, 0.55 g) was added. The mixture was stirred overnight before neutralizing with the saturated sodium carbonate. The product (Yield: 0.69 g, 65 %) was obtained by filtration and washed with water. EI MS: $m/z = 529$ [M+H$^+$]. IR (KBr, v/cm$^{-1}$): 1585(s), 1514(w), 1431(m), 1384(s), 1288(vs), 1087(vs), 781(vs), 766(vs), 748(vs), 729(vs), 652(s), 636(s). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.71 (d, 2H), 8.00 (t, 2H), 7.96 (s, 2H), 7.79 (d, 4H), 7.63 (s, 4H), 7.48 (d, 2H), 6.36 (s, 4H).

**Synthesis of [Cp$_2$Co][[(hfac)Co$_2$](b pptz)]$^-$ [hfac]$_2$$^-$Et$_2$O (1).** Treatment of Co(hfac)$_2$ (0.10 mmol, 0.047 g) and b pptz (0.05 mmol, 0.026 g) in CH$_2$Cl$_2$ solution (6 mL) at room temperature was followed by the addition of Co$_2$CO (0.05 mmol, 0.010 g) in CH$_2$Cl$_2$ (3 mL) under stirring. After the mixture was continuously stirred for 4 hours, the solvent was removed under vacuum, giving the brownish residue, washed by hexane (3 × 5 mL). The solid was then partially dissolved in Et$_2$O and filtered. The brownish block crystals of 1 were obtained via slow evaporation in two days, yield 0.011 g, 12 %. Anal. CalcCd Co$_3$H$_5$Co$_2$Ni$_4$OsO$_8$ (desolvated sample): C, 40.43; H, 2.06; N, 11.79%. Found: C, 40.12; H, 2.15; N, 11.44. IR (KBr, v/cm$^{-1}$): 1666(m), 1643(m), 1551(w), 1528(m), 1481(m), 1404(w), 1246(s), 1199(s), 1176(s), 1134(vs), 1014(w), 987(w), 937(w), 864(m), 783(m), 729(m), 659(s).

**Crystallography.** Single crystal X-ray diffraction (SC-XRD) measurement for 1 was performed at 160 K using a Bruker D8 VENTURE diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by the direct method of SHELXT and refined by full-matrix least squares (SHELXL) on $F^2$, and empirical absorption corrections (SADABS) were applied. Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. CCDC - 2085882 (1) contain the crystallographic data that can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk.

**Physical Measurements.** Elemental analyses (EA) (C, H, N, S) were measured by a vario elementar Automated Analyzer Analylysensysteme GmbH. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded in the range 600−4000 cm$^{-1}$ using a Bruker TENSOR II spectrophotometer. Magnetic susceptibility data were collected at temperatures between 2 and 300 K using a SQUID MPM53 magnetometer. Magnetic data were corrected for the diamagnetism of the sample holder; for the diamagnetism of the sample using Pascal’s constants.

**RESULTS AND DISCUSSION**

**Synthesis and Crystallographic Studies.** Complex 1 was prepared by the reaction of Co(hfac)$_2$ and b pptz in a 2:1 molar ratio in the presence of equivalent Cp$_2$Co as the reducing agent in dichloromethane. The SCXRD study revealed that 1 crystallized in the triclinic P$ar{1}$ space group (Table S1). The molecular structure of the [Co$_3$]$^+$ cation, as depicted in Figure 1, consists of two center symmetrically related Co(II) ions bridged by the b pptz ligand in the trans mode. Each Co(II) ion is located in a six-coordinate N$_2$O$_2$ environment formed by four N atoms from b pptz and two O atoms from hfac. The Ballar twist angle (φ) is 25.40°, and the deviation parameter (c) is calculated as 3.45 from an ideal D$_{6h}$ symmetry (c = 0), suggesting a distorted trigonal prismatic geometry. The metric values of Co−N/O bond distances are in the range of 2.053(1)−2.145(2) (Table S2), consistent with those reported for high-spin Co(II) species. This result was further supported by the Bond valence sum (BVS) calculations. Notably, an important structural characteristic for 1 is found by the significant elongation of intra-tetrazine N−N bond distance (1.383 Å) than those expected for the neutral form (~1.33 Å). Such elongation is consistent with the unpaired electron being located in the π* orbital of the tetrazine unit that has been widely observed for other compounds containing a tetrazine radical bridging...
ligand. For the packing arrangement, the [Co₃]⁺ cations are well isolated by the interstitial counterions with the nearest inter Co−Co separation being 9.7 Å; intermolecular interaction, if any, should be negligibly small (Figure S1).

**Figure 1.** Left: molecular structure of the [Co₃]⁺ cation in 1. All the hydrogen atoms, lattice solvents and counterions are omitted for clarity. Right: the TPR coordination environment of Co1 with the defined Bailar twist angle (θ).

**Magnetic Studies.** The magnetic susceptibility data for 1 was measured in the 2-300 K temperature range under an applied direct current (dc) field of 1 kOe (Figure 2). The $\chi T$ product of 5.02 cm$^3$ K mol$^{-1}$ at 300 K is higher than the expected spin-only value (4.125 cm$^3$ K mol$^{-1}$) for two isolated Co(II) ions ($S = 3/2$, 1.875 cm$^3$ K mol$^{-1}$) and a bptpz$^+$ radical ($S = 1/2$, 0.375 cm$^3$ K mol$^{-1}$), indicating the unquenched orbital contribution. Up cooling, the $\chi T$ product continuously increases to a maximum of 5.76 cm$^3$ K mol$^{-1}$ at 54 K, suggesting either the ferromagnetic interaction between the radical and two Co(II) centers, or the antiferromagnetic Co-radical coupling leading to the overall ferrimagnetic phase; it then decreases abruptly to 4.42 cm$^3$ K mol$^{-1}$ at 2 K, mainly attributed to the magnetic anisotropy of the metal centers. In terms of those similar tetrazine-radical bridged Co(II) compounds which exhibit the strong Co-radical antiferromagnetic coupling due to the overlap of Co-based $d_{xz}$ orbital and the π* orbitals of the radicals, the high-temperature increase of the $\chi T$ products in the current case is most likely explained via an antiferromagnetic Co-radical mechanism, and this is further supported by the theoretical calculations (*vide infra*). The isothermal field ($H$) dependence of the magnetization ($M$) was measured at 2−5 K, the lack of saturation ($M = 3.57$ Nμ at 7 T and 2 K) and the significant separations between the isofield curves (Figure S2) further confirm the presence of magnetic anisotropy. Based on the structural analyses, a magnetic model containing metal-radical centers and the coupling strength between the spin centers.

The best fit was achieved as follows: $U = 69$ cm$^{-1}$, $r_0 = 8.0 \times 10^{-12}$ s, $C = 3.0 \times 10^{-4}$ K$^{-0.8}$ s$^{-1}$, and $n = 8.8$. These results indicate...
that the Orbach and Raman processes dominate the relaxation of magnetization.

![Graph](image)

**Figure 3.** (a) Out-of-phase ac susceptibility data for 1 under 1.5 kOe dc field, the solid lines are guides for the eye. (b) The Arrhenius plot of 1, the red and green lines represent the high-temperature and overall fittings, respectively as discussed in the text.

**Theoretical Studies.** Single-ion anisotropy parameters for the individual Co(II) ions were first estimated using the *ab initio* CASSCF/NEVPT2 calculations (ORCA suite) based on the model extracted from the X-ray structure of 1 (Figure S10). The calculated parameters ($D = -42.6$ cm$^{-1}$, $g_{\|}/g_{\perp}/g_{\text{ax}} = 2.085/2.163/2.635$) are found to be in good agreement with those from the experimental data (Table 1). The calculations suggest the presence of strong axial anisotropy for the Co(II) ions with the dominant ground and first excited states with the electronic arrangements as \{($d_{x^2}$)$^2$(($d_{y^2}$)$^2$)$^2$($d_{z^2}$)$^2$($d_{x^2-y^2}$)$^2$\} and \{($d_{x^2-y^2}$)$^2$($d_{y^2}$)$^2$($d_{z^2}$)$^2$($d_{x^2}$)$^2$\}, respectively. The largest contribution to the negative and large $D$ parameter comes from the transition from the ground to the first excited state, mainly involving the magnetic orbitals of $d_{x^2-y^2}$ $\rightarrow$ $d_{x^2}$ with the same magnetic quantum number (m) and the smallest energy separation (Figure 4a, and Table S5). It is important to mention that the estimated transverse component of anisotropy ($|J| = 3.8$ cm$^{-1}$) for the Co(II) ions are found to be significantly high, suggesting a higher probability of ground-state QTM at single ion level.

To further support it, we also perform *ab initio* CASSCF + RASSI-SO$^{28}$ + SINGLE_ANISO$^{29}$ calculations on the same single-ion model from the X-ray structure of 1 using the MOLCAS suite.$^{29,29L,30}$ The sign and magnitude of the calculated anisotropy parameters for Co(II) ions (Table 1, $D = -54.5$ cm$^{-1}$, $g_{\|}/g_{\perp}/g_{\text{ax}} = 2.108/2.197/2.774$) are found to be in agreement with the CASSCF/NEVPT2 calculated values as well as the fitting results from the experimental data. Again, the calculated transverse component of anisotropy concerning the ground state QTM and the Orbach process which relates to the ground and the first excited states of opposite magnetizations are estimated to be large ($2.0 \times 10^{-1}$ $\mu_B$ and $9.7 \times 10^{-1}$ $\mu_B$ respectively, Figure 4b), suggesting that the relaxation via the ground state at a single-ion level.

In order to understand the overall behavior, we have considered both the Co(II)-radical and Co(II)-Co(II) exchange couplings in the CASSCF calculations. We use the POLY_ANISO program, which employs the Lines model$^{31}$ to fit the experimental susceptibility data, using the *ab initio* computed parameters from the Co(II) single-ion and $g = 2.000$ for the radical (s-tetrazine). The exchange Hamiltonian used for 1 is given by eqn. 3.

$$\hat{H}_E = -2J\hat{S}_{\text{rad}}(\hat{S}_{\text{rad}} + \hat{S}_{\text{rad}}) - 2J\hat{S}_{\text{rad}}\hat{S}_{\text{rad}} \ldots \ldots \text{eqn. 3}$$

Here, $J_1$ and $J_2$ describe the magnetic exchange interaction between Co(II)-radical and Co(II)-Co(II), respectively. The calculations (Figure 4c) nearly reproduced the experimental plot with the Co(II)-radical interaction of $J_1 = -59.8$ cm$^{-1}$, in good agreement with that extracted from the experimental data (*vide supra*). In addition, the DFT calculations on 1 affirmed that the strong AF interaction between the Co(II)-radical led to an $S = 5/2$ ground spin state (Table S6). The DFT computed spin density suggests dominant spin delocalization on the Co(II) centers with the spin density of 2.749 (Figure 4d, S11) and the singly occupied π*-s-tetrazine radical orbital is energetically close to the Co(II) 3d-orbitals. Furthermore, the overlap integral ($|S_{\text{rad}}|$) calculations using the singly occupied ligand and metal-based molecular orbitals demonstrated that out of the three possible Co(II)-radical(s-tetrazine) interactions, one of the interaction is really strong (Co(3d$_z$)||Rad(π*) = 0.218, Figure 4e and S12), dominating the strong AF interaction. It should be mentioned that both the DFT and *ab initio* calculations suggest the presence of small AF interaction between the Co(II) ions, as stated previously in several related complexes.interestingly, the exchange ground state QTM in 1 was found to be much smaller than the Co(II) single ion (0.086 $\mu_B$ vs. 0.20 $\mu_B$, respectively, Figures 4b and 4d). Apparently, the presence of strong exchange may effectively suppress the QTM effect. The first exchange excited state, on the other hand, has relatively high QTM probability (TA-QTM = 6.7 $\times$ 10$^{-1}$ $\mu_B$), suggesting the relaxation via the first excited state, giving the calculated energy barrier for spin reversal ($U_{\text{cal}}$) value of 100.7 cm$^{-1}$. Even though the estimated exchange ground state QTM is found to be smaller but not small enough to quench the QTM effect totally and thus the noted difference between the experimental and calculated barrier heights. Besides, other factors such as hyperfine coupling, intermolecular interactions etc. are also expected to add up to the overall relaxation process and the difference between $U_{\text{cal}}$ and $U_{\text{ref}}$.

With our recently reported trinuclear [Co-Co-Co] analogue, the incorporation of tetrrazine radicals in this case clearly engender much stronger magnetic interactions between metal ions and the radicals; the effective energy barrier for spin reversal is almost doubled and among the largest reported for polynuclear transition metal SMMs. This situation notwithstanding the considerable QTM effect of the Co(II) ions prevails the relaxation processes leading to the modest SMM behavior, most likely attributed to the geometric distortion from the ideal trigonal prismatic configuration. In this respect, further attempts towards restricting the trigonal prism geometry in this system seem to be critical.
Table 1. CASSCF fitted (MOLCAS suite) J values along with the SH parameters extracted from CASSCF/NEVPT2 for 1.

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<th>NEVPT2 (ORCA suite)</th>
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<tr>
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<td>$J_2$ cm$^{-1}$</td>
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Figure 4. (a) NEVPT2 computed d-orbital splitting along with dominant electronic transition (Red arrow); (b) CASSCF computed magnetic blockade diagram for Co(II) ion; (c) best fit for the $\chi^2$ vs T for 1 using POLY_ANISO along with the magnetic exchange values (black = exp. and red = fit); (d) DFT computed spin density plot for 1 with isodensity surface corresponding to 0.003 e Bohr-3; (e) dominant magnetic orbital interaction for 1 and (f) the ab initio POLY_ANISO computed magnetic blockade diagram for 1. In Figure b and f, the x-axis indicates the magnetic moment of each state along the main magnetic axis and the y-axis denotes the energy of the respective states. Thick black lines indicate Kramer’s doublets as a function of the magnetic moment. The green and blue lines indicate possible pathways of the Orbach and Orbach/Raman (O/R) contribution to the magnetic relaxation, respectively. The black transparent arrows indicate the most suitable relaxation pathway for magnetization reorientation. The red lines correspond to the QTM/TA-QTM relaxation pathways. The numbers provided at each arrow are the mean values for the corresponding matrix element of the magnetic moment.

CONCLUSION

In summary, a well-designed dual-capping tetrazine ligand of bpptz was synthesized and utilized for the construction of a novel dicobalt(II) SMM, in which the cobalt ions are caged within the distorted trigonal prismatic geometries and bridged by the tetrazine radical of the bpptz* ligand in trans mode. Magnetic and theoretical studies revealed the strong metal-radical coupling ($J_{\text{Co-rad}} = -65.8$ cm$^{-1}$), and considerable uniaxial magnetic anisotropy ($D_{\text{Co}} = -49.6$ cm$^{-1}$), giving an effective energy barrier of 69 cm$^{-1}$, among the largest for polynuclear transition metal SMMs. DFT and ab initio calculations suggest that the strong Co(II)-radical coupling effectively lower the ground-state quantum tunnelling half the order of magnitude compared to the Co(II) single ion. Efforts towards manipulating the radical-bridged metal ions within ideal trigonal prismatic geometries may lead to significant enhancement of the SMM property, and this work is in progress.

ASSOCIATED CONTENT
Supporting Information
An Exchange-Coupled [Co₂Cu] System, Exchange Couplings Drastically Slow Down Magnetization Relaxation in an
...and single molecule magnetism in redox-active tetraoxolene -
...Rechkemmer, Y.; Breitgoff, F. D.; van der Meer, M.; Atanasov, M.; Hakl,
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...Main Group Chemistry at the Interface with Molecular Magnetism,
...X-ray crystallographic data, selected bond lengths and angles,
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...bond lengths and angles, crystal structures, and magnetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interests.

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A dicobalt(II) single-molecule magnet consists of two trigonal-prismatic Co(II) blocks bridged by the tetrazine-radical is reported.