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Coligand effects on the architectures and magnetic properties of octahedral cobalt(II) complexes with easy-axis magnetic anisotropy

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Two mononuclear azido-cobalt(II) complexes, with formulas $[Co(3,3-Hbpt)_2(N_3)_2(H_2O)_2]$ (1) and $[Co(abpt)_2(N_3)_2]\cdot H_2O$ (2) (3,3-Hbpt = 1H-3,5-bis(3-pyridyl)-1,2,4-triazole, abpt = 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole), have been prepared by alternating the pyridyl-triazole coligands. In both complexes, Co(II) centers feature hexa-coordinated environments with distorted octahedrons in which the axial sites are identical, whereas the equatorial environments are finely modulated by the varying chemical natures of the different coligands. It is worth noting that the distinct intermetallic distances in two complexes (10.302 Å for 1 and 6.576 Å for 2) unambiguously cause the disparity of intermolecular interactions, implying the dissimilar magnetic behaviours. As a result, alternating current dynamic susceptibility measurements show that only 2 exhibits field-induced slow relaxation of the magnetization with an effective energy barrier of 11.29 K, though large easy-axis magnetic anisotropies for both complexes are unveiled by the combined analyses of the magnetic data and the *ab* initio calculations.

Introduction

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Single-molecule magnets (SMMs) have boundless prospects and could be considered as admirable models for comprehending quantum phenomena in the mesoscopic world and have promising potential for high-density magnetic information storage and quantum computation.¹ Such materials containing a unique slow-relaxing metal ion (the so called single-ion magnets (SIMs)) are an emerging class of SMMs that possess a crucial preponderance for tuning zerofield splitting (ZFS) through the regulation of the coordination number and ligand field of the coordination centers.² After the initial work on lanthanoid-based SIMs,3 the focus for the experimental and theoretical analysis of SIMs shifted to also include transition metals since Long and coworkers reported a mononuclear Fe(II) complex in a trigonal pyramidal geometry in 2010,⁴ and the SIMs of 3d transition metal ions have then endlessly emerged.⁵⁻⁸ Among them, monometallic cobalt(II)-

indefinable.

consequently enhancement of the anisotropy energy barrier (U_{eff}) of SIMs.¹² Moreover, the single Co(II) ion is very appealing since they offer the possibility to conserve the highly anisotropic nature of the individual spins while potentially reducing QTM through appropriate magnetic coupling and

suitable applied magnetic field. Therefore, fine-tuning the

containing complexes are explored the most because they are

air-stable in various cases. More importantly, such cases govern strong magnetic anisotropy attributed to significant

spin-orbit coupling in diverse geometric symmetries.9 For a

series of mononuclear Co(II) complexes, strong magnetic

anisotropies with both a negative ZFS parameter D (D < 0) and

an easy-plane anisotropy (D > 0) were clarified, exactly as Ruiz,

Luis, and co-workers proposed that, for a Kramers ion of

strong magnetic anisotropy, the field-induced slow magnetic

relaxation seemingly has no inevitable relation to the sign of

the D values.¹⁰ In light of this aforementioned situation, the

slow magnetic relaxation mechanism for Co(II) SIMs is still

In principle, the magnetic behaviour of SIMs primarily arises

from the inherent magnetic anisotropy of the metal center,

which is strongly impacted upon by the ligand field and



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Electronic Supplementary Information (ESI) available: Figures S1-S7, Tables S1-S9, crystal structures of 1 and 2 in CIF format. CCDC numbers are 1963359 (1) and 1963361 (2). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

coordination geometry as well as the coordination environment.¹¹ So far, reported examples have proven that fine-tuning of the coordination microenvironment through the modification of some structural factors, including the replacement of a substituent in a ligand, the ligand-field strength, counter anion nature and structural isomerism, can effectively contribute to a large magnetic anisotropy, and consequently enhancement of the anisotropy energy barrier

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structure of ligands is one of the possible influencing factors in modulating the ligand fields and intermolecular interactions as well as improving the anisotropy barriers for magnetic properties of Co²⁺ complexes. In the context, we focus here on the bent ligands which introduce 1H-1,2,4-triazole and 4-amino-1,2,4-triazole moieties between the two pyridyl groups and change the position of the pyridyl N atoms. The different degrees of bending which are caused by the diverse N atom positions could be conducive to the formation of different structures and, moreover, may give an antisymmetric interaction between the spin carries.¹³

Along with our investigation in this field, we have reported mononuclear Co(II) complexes, two new [Co(3.3- $Hbpt_{2}(N_{3})_{2}(H_{2}O)_{2}$ (1) (3,3-Hbpt = 1H-3,5-bis(3-pyridyl)-1,2,4triazole) and $[Co(abpt)_2(N_3)_2] \cdot H_2O$ (2) (abpt = 4-amino-3,5performing bis(2-pyridyl)-1,2,4-triazole), different architectures. The Co(II) centers of both complexes are indicative of distorted octahedral geometries, in which the axial sites occupied by azido moieties remain very similar to each other, whereas the equatorial environments are finetuned by different pyridyl-triazole coligands. Magnetic measurements reveal that easy-axis magnetic anisotropies (D < 0) are observed in both cases, which are further confirmed by ab initio calculations. However, only complex 2 presents field-induced slow magnetic relaxation.

Experimental

Physical Measurements

Elemental analysis (C, H, N) was implemented on a PerkinElmer 2400 CHN elemental analyzer. The FT-IR spectra were conducted in the range 400-4000 cm⁻¹ using KBr pellets on an EQUINOX55 FT/IR spectrophotometer. The phase purity of the polycrystalline samples was recorded by powder X-ray diffraction (PXRD) measurements performed on a Rigaku RU200 diffractometer at 60 kV, 300 mA and Cu K α radiation (λ = 1.5406 Å), with scan speeds of 2° min⁻¹ for 1 and 5° min⁻¹ for 2 and step size of 0.02° in 2 ϑ . Magnetic measurements on polycrystalline samples of 1 and 2 were accomplished using a Quantum Design MPMS-XL7 superconducting quantum interference device (SQUID) magnetometer (restrained in eicosane to prevent torquing under high fields). The measured magnetic data were corrected for the diamagnetism of the constituent atoms using Pascal's tables.

Materials and general procedures

All reagents were obtained from commercially available sources and used as received unless otherwise noted. 1H-3,5-bis(3-pyridyl)-1,2,4-triazole and 4-amino-3,5-bis(2-pyridyl)-1,2,4-triazole were synthesized following the previously reported method (Scheme 1).¹⁴



Scheme 1 syntheses of 3,3-Hbpt (a) and abpt (b).

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Caution! Although we have not encountered any problems in our experiments, azido and its complexes are posterially explosive; only a small amount of the materials should be prepared and disposed with care.

Synthetic procedures of 1 and 2

Synthesis of $[Co(3,3-Hbpt)_2(N_3)_2(H_2O)_2]$ (1). The hydrothermal method was adopted to synthesize the coordination polymer. A mixture of Co(NO₃)₂·6H₂O (0.0291 g, 0.1 mmol), 3,3-Hbpt (0.0446 g, 0.2 mmol), NaN₃ (0.0130 g, 0.2 mmol) and water (6 mL) was sealed in a 15 mL Teflon-lined stainless-steel vessel and heated at 140 °C for 3 days and then cooled to room temperature at a rate of 5 °C h⁻¹. Pink block crystals of 1 were collected in a yield of 69% (based on Co). Anal. calcd for C₂₄H₂₂CoN₁₆O₂ (*M* = 625.51): C, 46.09; H, 3.55; N, 35.83. Found: C, 46.02; H, 3.52; N, 35.80. IR (KBr, cm⁻¹): 3423 (s), 2976 (w), 2922 (w), 2083 (m), 1627 (m), 1472 (w), 1417 (w), 1381 (m), 1043 (m), 989 (w), 706 (w).

Synthesis of [Co(abpt)₂(N₃)₂]·H₂O (2). 2 was prepared in the same way as **1**, except that 3,3-Hbpt was substituted with abpt (0.0476 g, 0.2 mmol). Brown crystals were obtained (yield: 65%, based on Co). Anal. calcd for $C_{24}H_{22}CON_{18}O$ (M = 637.53). **2**: C 45.22, H 3.48, N 39.55. Found: C 45.19, H 3.44, N 39.52. IR data (KBr, cm⁻¹): 3441 (s), 3058 (w), 2046 (s), 1636 (m), 1600 (m), 1490 (w), 1454 (m), 1345 (w), 1253 (w), 788 (m), 697 (m), 606 (w).

Crystallographic data collection and refinement

Suitable single crystals of complexes **1** and **2** were selected for indexing, and the intensity data were recorded on a Bruker Smart APEX II CCD diffractometer equipped with a graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å) source. Using Olex2,¹⁵ the structures of **1** and **2** were solved with the ShelXT¹⁶ structure solution program using intrinsic phasing, and refined with the ShelXL¹⁷ refinement package using least squares minimisation. All of the non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms of complexes **1** and **2** were located from difference maps using the program Olex2. Basic information pertaining to the crystal parameters and structure refinement is summarized in Tables S1, and selected bond lengths and angles are listed in Tables S2 and S3.

Results and discussion

Crystal structure of 1 and 2

X-ray analyses suggest that complexes **1** and **2** crystallize in the monoclinic system with *P*21/*n* space group (Table S1). Both complexes are mononuclear motifs where the Co(II) ions display hexa-coordinated environments with distorted octahedrons. As depicted in Fig. 1a, the Co(II) ion in **1** is surrounded by two N atoms from two 3,3-Hbpt ligands and two O atoms from two water molecules that lie on the equatorial plane, and two N atoms from two azido anions are located at the axial positions. The axial Co-N bond distances (Co1-N6 = 2.131 Å) are longer than the equatorial Co-O bond distances (Co1-O1 = 2.043 Å) and a little shorter than

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equatorial Co-N bond distances (Co1-N1 = 2.175 Å). It is worth noting that the metal centers are well-separated with a shortest Co···Co distance of 10.302 Å, thus excluding potential intermolecular dipole-dipole interactions. In contrast, the metal center in **2** is chelated by two bidentate abpt ligands and two azido ligands, thus completing the CoN₆ coordination group. In **2**, the axial average Co-N bond distances (Co-N = 2.132 Å) are longer than the equatorial Co-N bond distances (Co-N = 2.117 Å). The smallest intermetallic distance in **2** is 6.576 Å, which illustrates nonnegligible intermetallic interaction. Additionally, π - π interactions between bpy rings exist in **1** and **2**, yielding three-dimensional supramolecular structures (Fig. S2 and S3).



Fig. 1 The asymmetric unit of the Co(II) ions in the complexes **1** (a) and **2** (b), showing the octahedral geometry around the Co(II) ion. H atoms and free H_2O molecules are omitted for clarity.

To ascertain the precise geometries around the metallic centers and the degree of the distortion from the ideal model for two complexes, the geometric spheres of Co(II) cations are calculated by using the SHAPE 2.1 program¹⁸ in the light of the crystal parameters, and the representative coordination polyhedrons are illustrated in Fig. 1. As listed in Table S4, the calculated values suggest that the Co(II) ions in both **1** and **2** represent octahedral (OC) geometry with tiny irregulars from the optimal geometry. The shape measure values for the octahedral polyhedrons are 0.219 for **1** and 0.886 for **2**, respectively. The relatively large value for the Co(II) ion in **2** corresponds to more deviation from ideal octahedral geometry.

In addition, the purity of the crystalline powders of **1** and **2** was measured by powder X-ray diffraction (PXRD) (Fig. S1). The experimental PXRD patterns of **1** and **2** are in accord with the corresponding simulated patterns obtained from the single-crystal data, confirming the high purity of the crystal samples.

Magnetic studies

Under a direct current (DC) field of 1000 Oe, the $\chi_{\rm M}T$ products at 300 K are 2.68 cm³ K mol⁻¹ for **1** and 2.92 cm³ K mol⁻¹ for **2** (Fig. 2), which are clearly larger than the spin-only value (1.875 cm³ K mol⁻¹) for a magnetically isolated Co(II) cation (*S* = 3/2 and *g* = 2.0), indicating a significant orbital contribution to the magnetic moment. Upon cooling, the $\chi_{\rm M}T$ values decreases

monotonously to 2.0 K, reaching 1.18 cm³ K molting for 1. The $\chi_{\rm M}T$ decrease of values is concurrently due 1070/spin or bit coupling of Co(II) ion and/or intradimeric antiferromagnetic coupling between Co(II) ions. Interestingly, for complex 2, as the temperature is lowered, $\chi_{\rm M} T$ first decreases smoothly to 2.65 cm³·K·mol⁻¹ at 20.0 K, then increases sharply to 2.81 cm³·K·mol⁻¹ at 14.0 K, and finally rapidly drops to 1.72 cm³·K·mol⁻¹ at 2.0 K. Although such curve rarely appeared in mononuclear Co(II)-SIMs, it could also be observed for a small number of known Co(II)-containing complexes with the similar situation.¹⁹ The high-temperature magnetic behaviours indicate that the magnetic interactions between Co(II) ions are dominated by antiferromagnetic coupling and/or a significant spin-orbit coupling, whereas this upturn at low-temperature of $\chi_{\rm M}T$ clearly demonstrates the possibility of weak ferromagnetic behaviour due to the spin-canting.¹⁹



Fig. 2 Plots of $\chi_M T$ versus T for complexes **1** (a) and **2** (b). Inset: The experimental plots of M versus H/T at different temperatures. The solid lines show the best-fitting curves to the experimental data.

The field-dependent magnetizations in the form of the *M* vs. *H* plots for **1** and **2** are represented in Fig. S4. For both complexes, the *M* vs. *H*/*T* plots at different temperatures are not superimposed (Fig. 2, inset), clearly indicating the presence of significant magnetic anisotropy, which is derived from the strong spin-orbital coupling of the Co(II) ion.²⁰ In order to analyze the magnetic anisotropy, reliable ZFS parameters were obtained by simultaneously fitting the experimental $\chi_{M}T$ vs. *T* and *M* vs. *HT*⁻¹ curves using the *PHI* program²¹ based on the following spin Hamiltonian:

$$\hat{H} = \mu_B (g_x \hat{S}_x B_x + g_y \hat{S}_y B_y + g_z \hat{S}_z B_z) + D (\hat{S}_z^2 - S(S+1)/3) + E (\hat{S}_x^2 - \hat{S}_y^2)$$
(1)

where $\mu_{\rm B}$ is the Bohr magneton, *D* is the axial ZFS parameter, *E* is the rhombic or transverse ZFS parameter, *S* is the spin operator, and *B* is the magnetic field vector, respectively. The parameters *D*, *E*, and *g* were selected to correlate the data. For the $\chi_{\rm M}T$ versus *T* curve of **2**, the superposition of the experimental data and the fitting one is not perfect in measured temperature range. Therefore, the fitting for **2** is only performed in the high temperature, reaching a good effect. Meanwhile, both positive and negative signs of D are considered in the fitting processes. However, only the negative sign reduces the experimental data very well. The best fit values were: $D = -54.71 \text{ cm}^{-1}$, $|E| = 1.62 \text{ cm}^{-1}$, $g_{x,y} = 2.02$, $g_z = 2.35$ for **1**, and $D = -35.38 \text{ cm}^{-1}$, $|E| = 0.35 \text{ cm}^{-1}$, $g_{x,y} = 2.03$, $g_z =$

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2.50 for 2, respectively. The negative sign of the D values for both complexes illustrates easy axial magnetic anisotropy, which is consistent with those previously reported for a few Co(II) SIMs.²² Moreover, the close comparison of q tensor components (g_x, g_y, g_z) of the ground Kramers doublet between 1 and 2 reveals that complex 2 possesses a larger axial component g_z , pointing out the stronger uniaxiality of the magnetic anisotropy in 2.

For the purpose of probing the spin dynamics, ac magnetic susceptibility experiments were conducted at zero dc field at a frequency of 1000 Hz and temperature range of 2-15 K. No out-of-phase (χ_{M}) signals were observed for **1** and **2** until the temperature dropped to 2 K (Fig. S5). The absence of slow relaxation under the zero dc field should be attributed to quantum tunneling of the magnetization (QTM) which is likely mediated by hyperfine and/or dipolar interactions, since (quadratic) transverse anisotropy cannot mix the wave functions of the $\pm M_s$ level for non-integer spin systems with D < 0 in the strictly zero field.

In order to find a suitable applied magnetic field to suppress the QTM effect, the χ_{M} susceptibilities for both complexes at 2.0 K and 1-1000 Hz were measured under different dc fields. No $\chi_{\rm M}$ " signals were observed in complex **1**. The plots concerning the field dependence of the relaxation time at 2.0 K for complex 2 have been given in Fig. S6. A significant sharp peak at around 2000 Oe dc field indicates field-induced slow magnetic relaxation and the slowest relaxation operating in 2. Thus, 2000 Oe was used as an optimal applied field for 2, and in-phase and out-of-phase ac susceptibilities were clearly observed. Accordingly, ac susceptibility measurements were performed in the range of 1.8-15 K and at frequencies of 1, 10, 33, 100, 333, and 1000 Hz for 2 (Fig. 3). The downturn in both the χ' and χ'' susceptibilities in the low-temperature range and the appearance of obvious peaks for both indicate that the relaxation probability via the quantum pathway has been obviously weakened or suppressed below 7 K. The observed peaks of the χ'' signals mirror the coincidence of the applied ac field oscillation frequency with the relaxation rate. At the selected frequency, 2 goes through a maximum and the maxima shift to high temperature with increasing frequency, which is the nature of a superparamagnet.²³



Fig. 3 Temperature dependence of ac susceptibilities for complex 2 under a 2000 Oe dc field.



Fig. 4 Frequency dependence of ac susceptibilities for complex 2 under a 2000 Oe dc field.

For purpose of further exploring the dynamics of the magnetization of 2, the frequency dependencies of the alternating-current (ac) susceptibility were measured under an applied dc field of 2000 Oe. As shown in Fig. 4, the χ' and χ'' curves of 2 behave as frequency dependencies at highfrequency zone with the proceeding of warming, which illuminates the occurrence of slow relaxation process. Fitting the high-temperature data using the Arrhenius law τ = $\tau_0 \exp(U_{eff}/k_BT)$ affords the effective spin-reversal energy barrier (U_{eff}) and pre-exponential factor τ_0 (Fig. 5): U_{eff} = 8.38 K (5.81 cm⁻¹) and τ_0 = 5.03 × 10⁻⁶ s, which is in accordance with the expectant τ_0 of 10⁻⁶-10⁻¹¹ for SIMs.²⁴ The barrier value is much smaller than what we expected $(2|D| = 70.7 \text{ cm}^{-1})$, demonstrating that other relaxation process like Raman and/or direct processes may be included. Also, the $ln\tau$ vs. T^{-1} plot appears to have some degree of curvature, reflecting the influence of nonnegligible other relaxation processes in determining the relaxation rate. Sequentially, a model including three possible relaxation processes (direct, Raman and Orbach mechanisms)²⁵ is applied to expound this relaxation behaviour:

 $\tau^{-1} = AT + CT^{n} + \tau_{0}^{-1} exp(-U_{\rm eff}/kT)$ (2)

where the terms in eqn (2) represent the contributions of Direct, Raman or Raman-like and Orbach mechanisms, respectively. For the second term, n = 7 is expected for the Raman process in non-Kramers ions and n = 9 for Kramers ions, while n = 1-6 can occur for the optical acoustic Raman-like process.²⁶ As depicted in Fig. 5, the fitting reproduces the experimental data very well, resulting in the parameters A = 2213.2 K⁻¹ s⁻¹, C = 0.1097 K⁻⁶ s⁻¹, τ_0 = 3.83 × 10⁻⁶ s, $U_{\text{eff}}/k_{\text{B}}$ = 11.29 K, and n = 6 (fixed). It is observed that the low temperature region is probably dominated by a direct process, whereas the relaxation process at high temperature can be mainly attributed to an optical acoustic Raman-like mechanism. For Kramers ions, like Co(II), the direct and QTM relaxation processes in a given doublet state are forbidden in strictly zero field. However, nuclear-spin interactions, as well as a transversal magnetic field created by intermolecular interactions (which is proportional to the matrix element of the transversal magnetic moments between the two doublet states) split the doublet states, providing relaxation channels for direct and QTM processes.²⁹ The Cole-Cole plots based on frequency-dependent ac susceptibility data for 2 could be modeled by the Debye model (Fig. 6 and S7).²⁷ The obtained parameters (α) are in the range of 0.306-0.334 for **2** (Table S5),

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indicating a wide distribution of relaxation times for a single relaxation process.²⁸ Compared with 1, the field-induced slow relaxation observed in complex 2 may be tentatively explained by analysing the intermolecular interactions. These interactions can arise from spin-spin dipolar interactions, which vary approximately with the (μ^2/r^3) ratio, in which μ is the magnetic moment of the magnetic dipole and r is the nearest neighbour distance between magnetic dipoles. In complex 2, the shortest Co…Co intermolecular distance is shorter than that found for **1** and there exist $\pi \cdots \pi$ stacking interactions between the anthracene rings with distances between the bpy rings. These considerations seem to indicate that in 2 the intermolecular interactions are clearly stronger than in 1. In view of this, it would be reasonable to suggest that the presence/absence of large intermolecular interactions seems to switch on/off the field-induced mononuclear SMM behaviour in these two complexes. Nevertheless, this suggestion should be taken with caution as other factors such as the molecular arrangement in the crystal lattice, the crystal density, the speed of sound in the solid and the strength of the spin phonon interactions, and the possible change of the Co(II) coordination environment can influence QTM and spin-lattice direct and Raman relaxation process.



Fig. 5 Magnetization relaxation time, $\ln \tau vs. T^{-1}$ plot under 2000 Oe dc field for **2**. The red lines and green lines represent the Arrhenius fit and multiple relaxation processes, respectively.



Fig. 6 Cole–Cole plots under 2000 Oe for **2**. The solid lines show the best fitting according to the generalized Debye model.

Theoretical calculations

In order to obtain a better understanding of the slow magnetic relaxation of complexes **1** and **2**, the post-Hartree-Fock CASSCF calculations were performed. The ORCA 4.0.1 computation package³⁰ was utilized to perform CASSCF calculations³¹⁻³³ for

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CASSCF(7,5) using the scalar relativistic contracted wersion of def2-TZVP(-f) basis functions.³⁴ The approach dome with ORCA resulted in negative *D*-values (-72.15 cm⁻¹ for 1 and -37.21 cm⁻¹ for 2), which are comparable to the fitting values (-54.71 cm⁻¹ for 1 and -35.38 cm⁻¹ for 2). Although the calculated values show a slight deviation from the fitting values, the sign of the *D* constant matches well with the fitting ones, which definitely confirms the easy axis magnetic anisotropy of the complexes. This may result from the fact that the real complexes are not made up of scattered entities as they have been modelled, but are very complicated across the whole structures. The calculated effective g_z tensors are 2.8414 ($g_{x,y} = 2.0011$, 2.2857) and 2.5192 ($g_{x,y} = 2.0778$, 2.2470) for 1 and 2, respectively. The energy levels and the contributions of the excited spin states to *D*-tensor are listed in Tables S6-S9.



Fig. 7 AILF-computed d-orbital splitting for complexes 1 (a) and 2 (b).

The sign and value of D can be rationalized by using the spinorbit operator, which is responsible for the coupling between the ground and excited states.³⁵ When the excitation occurs between orbitals with the same $|m_1|$ values, the M_s = ± 3/2 components become more stable, and thus a negative contribution to the D value is obtained. On the other hand, an excitation between orbitals that involves a $|\Delta m_1| = 1$ change, which produces stabilized $M_{\rm S}$ = ± 1/2 components, leads to a positive contribution to the D value. Both complexes display distorted octahedral core that produce the d-orbital splitting shown in Fig. 7, which are obtained from the ORCA/CASSCF calculation by using the ab initio ligand-field theory (AILF).^{35a, 36} The AILF method allows the identification of the d orbitals in 1 after splitting, and the lowest-energy doubly occupied orbital is d_{z^2} , which is followed by the doubly occupied orbital d_{xy} , whereas the first semioccupied orbital is. The other two orbitals (d_{xz} and d_{yz}) are found at higher $d_{y^2-y^2}$ energies. In the case of complex $\boldsymbol{2},$ the last doubly occupied orbital is d_{z^2} and the first semioccupied orbital is $d_{\mbox{\scriptsize yz}}.$ The observed difference in the orbital ordering between 1 and 2 arises due to the difference in the metal-ligand interaction. Thus, the first excitation should occur within the $d_{xy}/d_{x^2-v^2}$ orbital pair for 1 and d_{z^2}/d_{vz} orbital pair for 2, because these orbitals have same $|m_{\rm I}|$ value, the larger contribution to the D value should be negative; consequently, the magnetic easy-axis nature of 1 and 2 are confirmed.

Conclusions

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In this work, the coligand effect on the magnetic behaviour of the Co(II) center in stretched octahedral geometry has been investigated. To eliminate other factors affecting the magnetic anisotropy, we have chosen azido ligand to lie on the axial sites, leading to two air-stable cobalt(II) complexes which have almost the same axial environments, leaving the equatorial positions as the key variable on the magnetic behaviour. The easy-axis magnetic anisotropies of single mental ion in both complexes were confirmed by magnetic measurements and theoretical calculations. The difference of the shortest intermolecular Co---Co distances in two complexes (10.302 Å for 1 and 6.576 Å for 2) results in distinct intermolecular interactions, contributing to the divergence of the magnetic properties, that is, only complex 2 presents field-induced slow magnetic relaxation, characteristic of SIMs with anisotropy energy barrier of 11.29 K.

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Graphical abstract

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Synopsis

• Coligand effect leads to two mononuclear octahedral Co(II) complexes exhibiting easy-axis magnetic anisotropies and distinct magnetic properties.

Graphic

