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ARTICLE

Exposing the Intermolecular Nature of the Second Relaxation Pathway in a Mononuclear Cobalt(II) Single-Molecule Magnet with Positive Anisotropy.

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The investigation of a pentagonal bipyramidal Co(II) complex with large positive anisotropy ($D \approx +30$ cm^{-1}) revealed field induced Single-Molecule Magnet behaviour with $U_{eff} \approx 50$ K at 1.0 kOe. This compound belongs to a group of only a handful of complexes which exhibit this unique magnetic property while possessing easy-plane anisotropy. At high applied fields, a second relaxation process with an intermolecular nature has been exposed using magnetic dilution studies with varying percentages of Zn(II) analogue. The disappearance of the second relaxation process at low frequency can be followed using magnetically diluted samples at 25%, 10% and 5% Co(II) concentrations.

Introduction

Researchers have repeatedly stressed the necessity for information storage technologies which can overcome the fast-approaching limits of our current systems.[1] The search has thus far led to the active development of the field of Single-Molecule Magnetism where molecular entities have proven to be magnets exhibiting bistability and magnetic hysteresis with very long relaxation times, on the order of years at very low temperatures.[2] The recent surge in these nanomagnets, known as Single-Molecule Magnets (SMMs)[1,3] have yielded a pseudo-recipe for their design and isolation with desired properties, mainly high energy barriers for spin reversal (U) and high blocking temperatures (T_B).[4] The barrier for spin reversal has been quoted to depend linearly on the spin of the complex (S) as well as exponentially on its overall anisotropy (D for uniaxial or Ising-type and E for transverse or easy-plane anisotropy) where $U_{eff} = S^2|D|$ or $U_{eff} = (S^2-1/4)|D|$ for integer and half-integer spins, respectively. Thus far, there have been significant advancements in the field with extremely large energy barriers being reported as well as relatively high blocking temperatures[4] (up to 14 K[4a] for a dinuclear lanthanide complex). While higher nuclearity clusters were previously pursued, it is now believed that the anisotropy of a complex is the main contribution towards a high energy barrier.[5] Moreover, as the cluster increases in size with more anisotropic metal centres, the overall anisotropy of the compound will inherently decrease as it is more difficult to align all the easy-axes in one direction. Hence, mononuclear complexes have been sought

after as the simplest nanomagnets, especially those with high magnetic anisotropy such as high spin Co(II)- or Fe(I)/(II)/(III)-based complexes.[4e,6]

Furthermore, recent advances in this field have led to the isolation of extremely rare complexes exhibiting slow magnetic relaxation characteristic of SMMs while possessing positive or easy-plane anisotropy (positive D values).[5c,7] It is not well-understood how these complexes can behave as SMMs when their lowest sublevel of the spin ground state is stabilized. This behaviour has been attributed to a field-induced phonon bottleneck in a pseudotetrahedral Co(II) complex which generates Orbach relaxation through the $M_s = \pm 3/2$ levels and an energy barrier dependent on D.[7b] Meanwhile, another example of a six-coordinate Co(II) complex has been reported where the barrier to spin reversal is governed by the transverse anisotropy (E parameter) as opposed to D.[7a] We have chosen to focus on a seven-coordinate mononuclear Co(II) complex [Co(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$) (**1**, Fig. 1, DAPBH = 2,6-diacetylpyridinebis(2'-pyridylhydrazone)) with positive or easy-plane anisotropy.[8] This coordination number is known to result in large magnetic anisotropy due to the axiality of the resulting pentagonal bipyramidal geometry.[9] Furthermore, complex **1** exhibits interesting out-of phase magnetic behaviour at high applied fields, the origin of which remains relatively unknown. In order to investigate this rare relaxation process observed only at high applied fields we have employed systematic magnetic dilution using the diamagnetic Zn(II) analogue in 25, 10 and 5% Co samples.
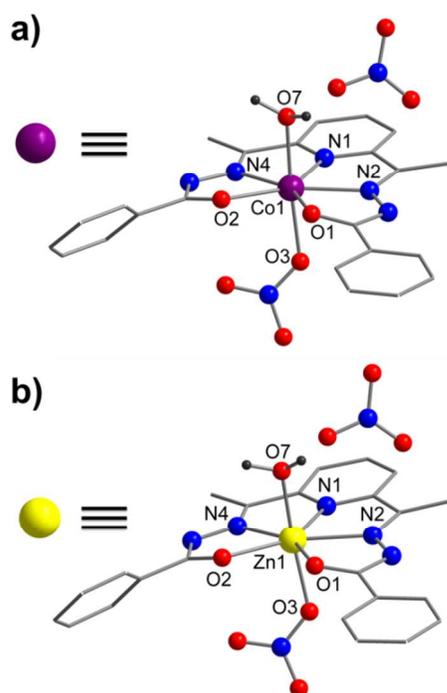
Figure 1. Molecular structures of [Co(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$) (**1**, a) and analogous complex [Zn(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$) (**2**, b). Hydrogen atoms on DAPBH are omitted for clarity. Colour code: Purple (Co), yellow (Zn), blue (N), red (O), grey (C), black (H).

This methodology has already proven successful in our study of the magnetic exchange interaction between Dy(III) ions in a dinuclear complex [Dy$_2$(valdien)$_2$(NO$_3$)$_2$] using the Y(III) analogue.[10] Hence, this strategy will allow us to elucidate the origin of the observed relaxation process at high fields by exposing its nature as intramolecular (intrinsic to the Co(II) ion in the mononuclear complex) or intermolecular where Co(II) ions in the lattice begin to interact magnetically.

Experimental Section

Materials
All manipulations were carried out under aerobic/ambient conditions. Chemicals were purchased from *TCI*, *Alfa Aesar*, and *Strem Chemicals*, and used without further purification.

Synthesis

2,6-diacetylpyridinebis(2'-pyridylhydrazone) (DAPBH): The ligand, DAPBH, was synthesized in accordance with a literature procedure.[8a]

[Co(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$), 1: This complex is synthesized following a procedure previously reported in the literature.[8a,b] Selected IR (cm^{-1}): 3401 (w), 3163 (br), 3201 (m), 2970 (w), 1630 (s), 1602 (w), 1578 (m), 1537 (s), 1492 (w), 1406 (m), 1319 (s), 1191 (m), 1136 (w), 1076 (w), 1043 (m), 1018 (w), 902 (m), 809 (s), 741 (s), 712 (s), 689 (m), 675 (w). Elemental Analysis; Expected: C 46.01%, H 3.87%, N 16.33%; Found: C 45.85%, H 3.70%, N 16.35%.

[Co$_{0.25}$Zn$_{0.75}$(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$), (25% Co(II) sample): To a solution of DAPBH (0.500 mmol, 0.199 g) in 5

mL H$_2$O was added a solution of Co(NO$_3$)$_2$·6H$_2$O (0.125 mmol, 0.036 g) and Zn(NO$_3$)$_2$·6H$_2$O (0.375 mmol, 0.112 g) in 10 mL of ethanol. The solution was heated to 80 C with stirring for 1 hr then allowed to cool down. The filtrate was allowed to stand at room temperature, and orange crystals were obtained after one day in 76% yield. Selected IR data (cm^{-1}): 3392 (w), 3155 (br), 3199 (m), 2972 (w), 1631 (s), 1602 (w), 1579 (m), 1537 (s), 1493 (w), 1406 (m), 1321 (s), 1193 (m), 1132 (w), 1078 (w), 1044 (m), 1017 (w), 899 (m), 809 (s), 742 (s), 711 (m), 690 (m), 675 (w). Elemental Analysis; Expected: C 46.01%, H 3.87%, N 16.33%; Found: C 45.65%, H 3.68%, N 16.24%.

[Co$_{0.10}$Zn$_{0.90}$(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$), (10% Co(II) sample): The synthetic procedure followed is the same as that mentioned above using Co(NO$_3$)$_2$·6H$_2$O (0.050 mmol, 0.015 g) and Zn(NO$_3$)$_2$·6H$_2$O (0.450 mmol, 0.134 g). Yield = 69%. Selected IR data (cm^{-1}): 3386 (w), 3149 (br), 3202 (m), 2969 (w), 1633 (s), 1602 (w), 1579 (m), 1534 (s), 1493 (w), 1406 (m), 1326 (s), 1192 (m), 1132 (w), 1075 (w), 1044 (m), 1018 (w), 901 (m), 809 (s), 744 (s), 713 (s), 691 (m), 673 (w). Elemental Analysis; Expected: C 46.01%, H 3.87%, N 16.33%; Found: C 45.64%, H 3.68%, N 16.26%.

[Co$_{0.05}$Zn$_{0.95}$(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$), (5% Co(II) sample): The synthetic procedure followed is the same as that mentioned above using Co(NO$_3$)$_2$·6H$_2$O (0.025 mmol, 0.007 g) and Zn(NO$_3$)$_2$·6H$_2$O (0.475 mmol, 0.141 g). Yield = 71%. Selected IR data (cm^{-1}): 3381 (w), 3150 (br), 3203 (m), 2966 (w), 1634 (s), 1602 (w), 1579 (m), 1535 (s), 1492 (w), 1405 (m), 1327 (s), 1191 (m), 1132 (w), 1076 (w), 1043 (m), 1017 (w), 899 (m), 809 (s), 741 (s), 712 (s), 689 (m), 673 (w). Elemental Analysis; Expected: C 46.01%, H 3.87%, N 16.33%; Found: C 45.71%, H 3.69%, N 15.94%. ICP analysis yielded 4.91% Co in the sample, in accordance with the 5% Co employed during the synthesis.

[Zn(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$), 2: The synthetic procedure followed is the same as that mentioned above for the various Co(II) samples, using only Zn(NO$_3$)$_2$·6H$_2$O (0.500 mmol, 0.149 g). Yield = 59%. Selected IR data (cm^{-1}): 3389 (w), 3159 (br), 3194 (m), 2970 (w), 1631 (s), 1602 (w), 1581 (m), 1535 (s), 1493 (w), 1406 (m), 1323 (s), 1190 (m), 1132 (w), 1079 (w), 1044 (m), 1015 (w), 898 (m), 809 (s), 743 (s), 711 (s), 689 (m), 674 (w). Elemental Analysis; Expected: C 46.01%, H 3.87%, N 16.33%; Found: C 45.62%, H 3.66%, N 15.96%.

Physical Measurements
Single crystal X-ray crystallography was carried out on a Bruker APEX-II CCD device which was used to collect unit cell and intensity data using graphite Mo-Kα radiation (λ = 0.71073). The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structures were solved and refined using the SHELXTL program suite.[11] Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms. Infrared spectra were recorded on solid samples on a Varian 640 FT-IR spectrometer in the 400-4000 cm^{-1} range. Elemental analyses were carried out at Canadian Microanalytical Service Ltd. Magnetic measurements were carried out using a SQUID MPMS XL7 magnetometer for direct current (dc) applied fields ranging from 7 to -7 T as well as temperatures ranging from 1.8 – 300 K. Alternating current

(ac) susceptibility measurements were performed under an oscillating ac field of 3.78 Oe and ac frequencies ranging from 0.1 to 1500 Hz. In order to check for ferromagnetic impurities, the magnetization data were collected at 100 K. No ferromagnetic impurities were detected in all samples measured. Diamagnetic corrections were applied for the sample holder and the diamagnetism from the sample which was estimated using with Pascal constants. Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES—730-ES, Varian Inc., Palo Alto, CA, USA) at the University of Ottawa, department of Earth Sciences, was employed to confirm the ratio of Zn:Co in the diluted sample. The 10.0 mg sample was digested by 1.0 ml conc. HNO_3 then diluted to 10 ml of final solution with distilled water. The standard solutions were prepared using $Co(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$.

Results and Discussion

The previously reported complex, **1**, is synthesized through the reaction of $Co(NO_3)_2$ and DAPBH in ethanol and H_2O.[8] It exhibits pseudo pentagonal bipyramidal geometry with the DAPBH ligand occupying the pentagonal plane while one nitrate anion and one water molecule occupy the axial positions (Fig. 1). The packing diagrams of the Co(II) units are shown in Fig. 2 along the *a*-, *b*- and *c*-axes with the closest Co(II)…Co(II) distance being 7.33 Å while the pentagonal planes of DAPBH are aligned in near parallel fashion with a distance between overlapping phenyl rings of 3.80 Å indicating $\pi…\pi$ interactions within the lattice (Fig. 3). These intermolecular interactions can facilitate magnetic communication between the highly anisotropic mononuclear Co(II) ions leading to interesting ac magnetic behaviour (*vide infra*).

The magnetic anisotropy of the Co(II) ion in **1** has been examined extensively by Guihéry, Mallah and co-workers[8b] using magnetization measurements, high-field high-frequency EPR measurements as well as *ab initio* calculations. This elegant study focused on the main origins of the large positive zero-field splitting parameter ($D \approx +30$ cm^{-1}) in this Co(II) complex compared with the Ni(II) analogue. The authors determined it was a result of the positive contributions arising from interactions of the excited states (two quartet and one doublet) with the ground state. All important contributions to the *D* parameter are shown to stabilize the $Ms = \pm1/2$ component as opposed to the $Ms = \pm3/2$ component of the $S = 3/2$ ground state. This essentially yields easy-plane anisotropy where the magnetization is in the plane of the DAPBH ligand perpendicular to the axial H_2O and NO_3^- ligands (Fig. 3). While previous reports have disregarded this complex as a potential SMM due to its positive anisotropy,[9b] we believe it is an appropriate system in which to study such novel phenomenon as it is quite rare with only a handful of articles published on SMMs with easy-plane anisotropy.[7] Additionally, it is not well-understood as of yet how these complexes exhibit bistability under an applied dc field.
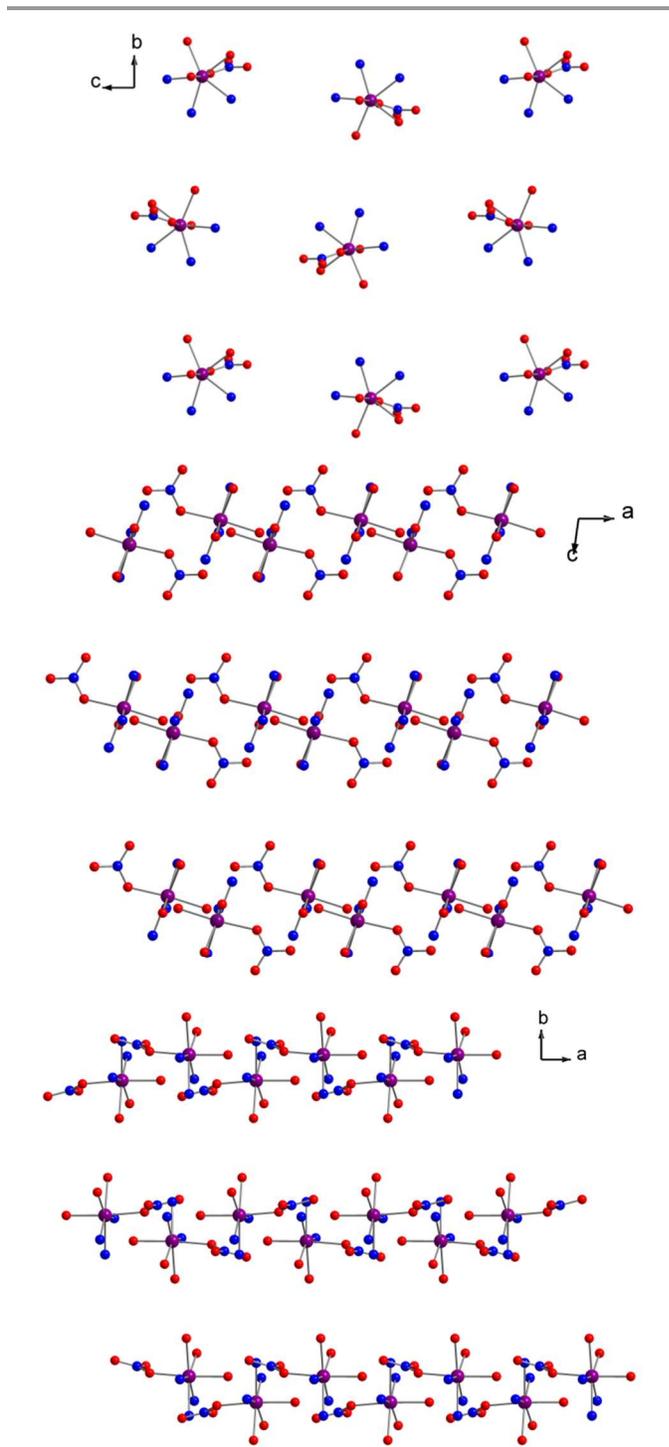
Figure 2. Packing diagrams of **1** along the *a*- (top), *b*- (middle) and *c*-axes (bottom). Colour code: Purple (Co), blue (N), red (O). Only the atoms directly coordinated to Co(II) centres, as well as the coordinated NO_3^- molecule are shown for clarity. Counter ions are omitted.

Contrary to previous reports concerning the SMM properties of complexes with mainly transverse anisotropy, complex **1** exhibits ac magnetic behaviour characteristic of molecular magnets under an applied static dc field. Alternating current (ac) magnetic measurements under an oscillating field of 3.78 Oe and static dc fields ranging from 0 to 8.2 kOe at 2 K

revealed a frequency dependent relaxation process in the in-phase (χ', Fig. S1-S4) and out-of-phase magnetic susceptibility (χ'') *vs.* frequency plot (Fig. 4 left, Process A). As the applied dc field increased, this process shifts to lower frequency reaching the minimum of the characteristic frequency at 1.0 kOe (optimal applied field minimizing QTM for this process). Upon further increasing the applied field, a shoulder begins to appear at lower frequencies starting at 2.8 kOe and increases in intensity as the applied field increases (Fig. 4 left, Process B). This second process has been relatively puzzling for researchers in the field, it has often been alluded to as a second relaxation pathway for the spin inherent to the Co(II) ion or, in other words, an intramolecular phenomenon depending solely on the Co centre.[6a,]
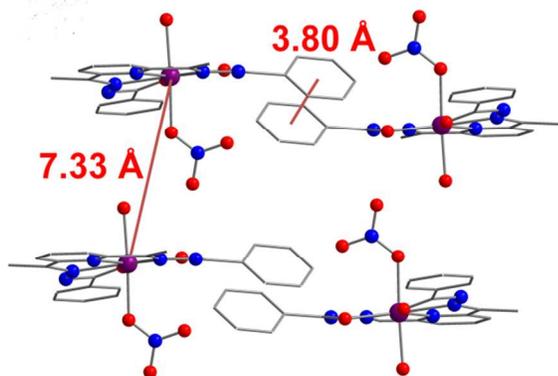
Figure 3. Intermolecular distances are shown between Co(II) centres as well as between phenyl rings indicating π…π interactions. Distances are indicated in red. Colour code: Purple (Co), blue (N), red (O).

In order to investigate whether the origins of this process are intramolecular or intermolecular in nature, we have designed an experiment using magnetic dilution of **1** with the diamagnetic Zn(II) analogue (**2**). It is noteworthy that the Zn(II) complex is identical to **1** which is important in order for the two to co-crystallize and the only changes observed then are in the magnetic behaviour as opposed to the overall lattice structure. Different samples with varying percentages of Co(II) (25, 10 and 5%) were synthesized using the same procedure as the parent (100%) complex, **1**, as seen in the schematic diagram in Fig. 4, right, with Co centres shown as purple spheres (for synthetic details, refer to Experimental Section). As the samples become more diluted with Zn(II) (yellow spheres), the magnetic interactions between adjacent Co(II) ions become less likely to occur. This effectively reduces to a large extent the intermolecular interactions leaving only the intramolecular behaviour of the mononuclear Co(II) complex. In order to confirm the magnetically diluted samples are structurally identical to the parent compound, single-crystal X-Ray diffraction, elemental and Infra-Red analyses were performed (see Experimental Section). The obtained data was consistent with that of **1** confirming the structural integrity of all samples. As seen in Fig. 4, the decrease in the percent of Co(II) ions in the sample is followed by the decrease in intensity of process B at low frequency. By calculating the ratio of processes A:B at different percentages of Co we can track the decrease in B. Ratios of 1.16, 1.54, 2.83 and 3.89 were obtained for 100, 25, 10 and 5% Co(II) samples, respectively, meaning process A becomes more dominant with lower percentages of Co(II) ions while process B decreases significantly.
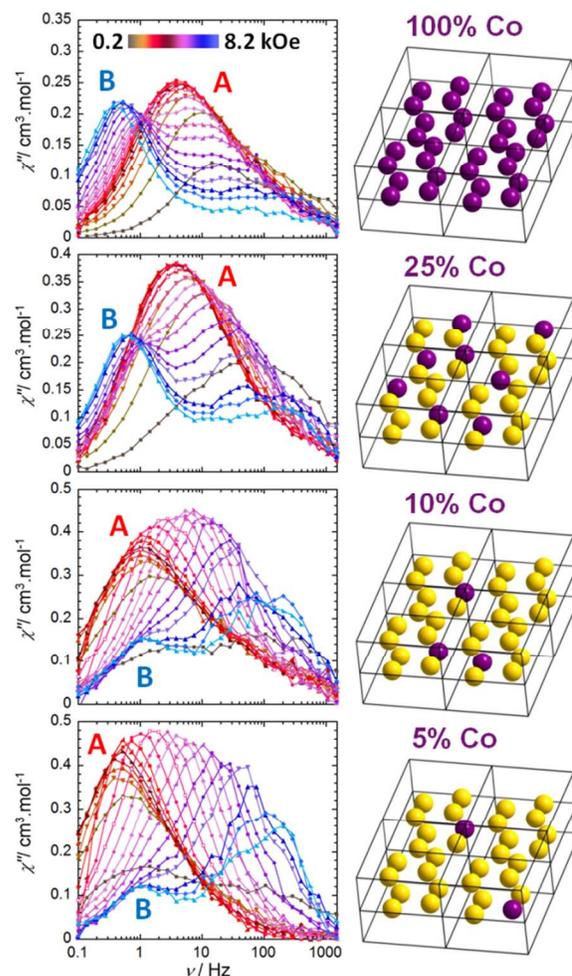
Figure 4. (Left) Out-of-phase (χ'') *vs.* frequency plots of the magnetically diluted samples. Measurements were performed between 0.2 and 8.2 kOe at a temperature of 2 K. A and B refer to the two relaxation processes discussed in the text. (Right) Schematic diagram of the magnetic dilution using the Zn analogue (complex **2**) with the percentage of Co ions indicated. Colour code: Purple (Co), yellow (Zn).

These data provide clear evidence to the intermolecular nature of process B, where at high applied dc fields, the Co(II) centres begin to interact with one another. This is contrary to previous reports attributing this lower frequency process to inherent properties of the metal centres leading to multiple relaxation processes within mononuclear complexes. When performing magnetic measurements at high applied dc field, one must be aware of this ordering that can occur due to intermolecular interactions yielding ac signals that can appear as molecular processes. It is worth noting, however, that the peaks associated with Process B, do not diminish completely as the sample becomes more magnetically diluted. This is due to the probability that some Co(II) complexes will remain in close proximity in different parts of the crystal lattice such that magnetic interaction can occur. Since the magnetically diluted sample is still crystalline, the probability of finding Co(II) ions adjacent to one another decreases but does not reach zero. By measuring χ'' as a function of frequency in the temperature range of 7 – 1.8 K at the optimum applied dc field for the Orbach relaxation process (1.0 kOe, Fig. 5), the energy barrier

to the reversal of the magnetization can be calculated (using the Arrhenius law, $\tau = \tau_0\exp(U_{\text{eff}}/kT)$). It is noteworthy that the optimum field of 1000 Oe was chosen for all samples in order to remain consistent such that comparable energy barriers could be obtained. Additionally, the intensities of the peaks in the ac plots are very similar since they were not calculated per Co centres but rather the molecular weight of the entire sample was used (Co and Zn).

The experimentally observed effective barrier of $U_{\text{eff}} = 50\text{-}55$ K for process A was found to be consistent among all magnetically diluted samples (Fig. 6) validating its intramolecular nature as well as confirming that the same process persists even at 5% Co(II) in the sample. This is significant as it confirms that Process A is relatively unaffected by the intermolecular interactions between neighbouring units rendering it purely molecular in origin. Had the energy barrier changed then it would have been clear that we are observing different relaxation processes but since it remained the same, it is indicative of the same relaxation mechanism in all diluted samples attributable to the Co(II) ion without the influence of intermolecular interactions.
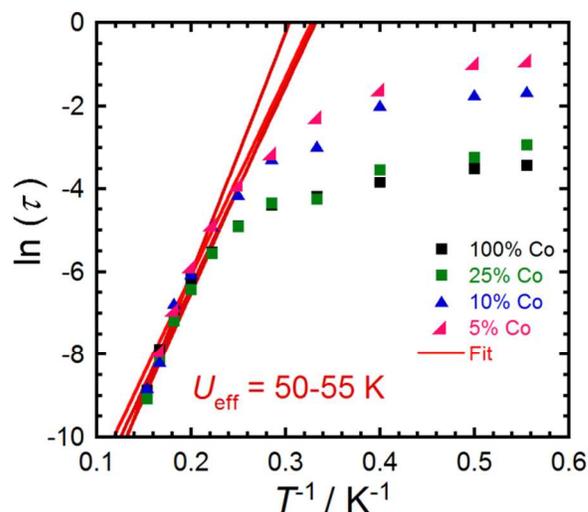
Figure 6. Relaxation time of the magnetization at 1.0 kOe plotted as $\ln(\tau)$ vs. $1/T$ for all magnetically diluted samples for process A. Fit lines are indicated in red.
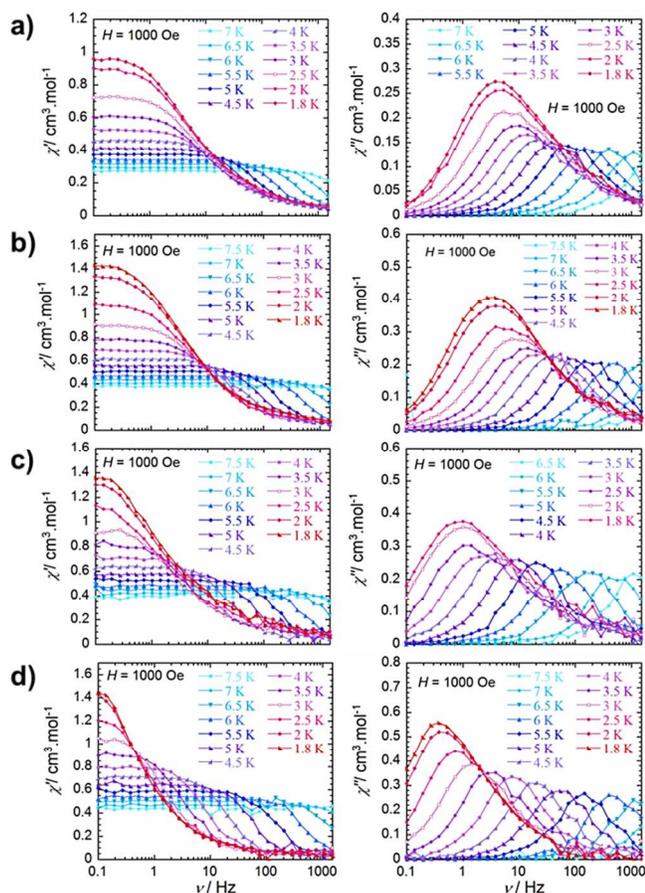
The observed magnetic relaxation behaviour for **1** could also be fit well to a power dependence on temperature which is indicative of operative Raman process where $\tau^{-1} = CT^n$ (Fig. S5). The best fit parameters obtained were $C = 4.66 \times 10^{-4}$ and $n = 8.6$ which is in accordance with expected values for Kramer ion SMMs where $n \geq 4$.[6h,12]

Conclusions

In summary, we have investigated the magnetic behaviour and SMM properties of a hepta-coordinate Co(II) complex with large positive anisotropy. The slow relaxation of the magnetization under an applied field of 1.0 kOe yielded an energy barrier for spin reversal of $U_{\text{eff}} \approx 50$ K. We are currently looking into other examples in the literature of such complexes which have been overlooked precisely because of their large positive D values. An interesting feature of the ac magnetic behaviour was explored using magnetic dilution studies. Using the diamagnetic Zn(II) analogue of **1**, we were able to determine that the relaxation occurring at high fields and low frequency was intermolecular in nature as opposed to an inherent property of the Co mononuclear unit. At high fields, these entities are no longer behaving as SMMs but rather interacting with one another within the lattice due to their highly anisotropic nature. This study has shown that high field measurements can be a double-edged sword; on the one hand it can provide vital information regarding the slow relaxation and QTM in a complex while on the other it can result in intermolecular interactions which are absent at low field. Furthermore, magnetic dilution studies can provide a unique solution to separating relaxation processes in addition to understanding their origins in a molecular system.

Figure 5. Frequency (ν) dependence of the in-phase (χ') and out-of-phase magnetic susceptibility, χ'', at the indicated applied field (H) and temperature ranges for **1** (a), 25% Co(II) (b), 10% Co(II) (c) and 5% Co(II) samples (d).

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Notes and references

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