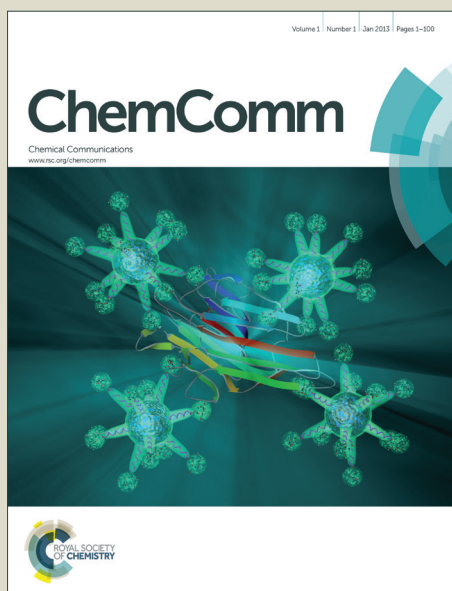


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COMMUNICATION

Synthetic Strategy for Switching the Single Ion Anisotropy in Tetrahedral Co(II) Complexes

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Four novel mononuclear tetrahedral cobalt(II) complexes containing exocyclic mesoionic ligands of molecular formulae $[\text{Co}^{\text{II}}(\text{L}_1)(\text{X})_2(\text{MeCN})]$ $\text{X} = \text{Cl}$ (1) or Br (2) and $[\text{Co}^{\text{II}}(\text{L}_2)(\text{X})_2(\text{MeCN})]$, $\text{X} = \text{Cl}$ (3) or Br (4) have been reported. It is found that by simple substitution of L_1 (O donor in 1 and 2) by L_2 (S donor in 3 and 4) results in switching of the single ion magnetic anisotropy parameter (D) from positive to negative, with a significant change in magnitude.

Following the discovery of single-molecule magnet (SMM) behavior in the famous $\{\text{Mn}_{12}\}$ cluster, the number of polynuclear transition metal complexes expanded rapidly to probe this phenomenon.¹ It was subsequently found, however, that problems arise for multinuclear transition metal clusters as the magnitude of the anisotropy D is found to be inversely proportional to S^2 , thus hampering the effort to find high temperature SMMs.² In 2003, slow magnetic relaxation was reported for a mononuclear lanthanide complex which displayed superior magnetic relaxation behavior compared to that of any transition metal complex.³ Following this observation, record blocking temperatures and anisotropic barriers were subsequently developed which were based on lanthanide single ion magnets (SIMs).⁴ On the other hand transition metal based SIMs are very scarce in the literature due to quenching of the orbital angular momentum by the ligand field. Low coordinate mononuclear transition metal complexes such as two coordinate Fe(I), Fe(II) and Ni(I) SIM complexes, however, have revealed a promising new approach towards SIM synthesis, where the maximum single ion anisotropy is harvested due to the unrestricted orbital angular momentum by limiting the coordination number of the metal ion.⁵

Among transition metal ions, Co(II) based complexes are particularly attractive towards blocking the magnetization as they possess a non-integer spin ground state,⁶ which reduces the possibility of quantum tunnelling of magnetization (QTM).⁷ The majority of reported tetrahedral Co(II) complexes, however, still require a bias dc magnetic field to observe SIM behaviour, except for two complexes, where the reported easy axis anisotropy (negative zero-field splitting; zfs) values are significantly large in magnitude.⁸ This implies that the single ion anisotropy associated

with the complex needs to be increased drastically.⁹ While significant experimental and theoretical efforts have been undertaken, a rational approach to fine tune the axial zfs parameter, D , of mononuclear complexes has yet to be achieved. With this in mind, we set out to investigate possible means to modulate the magnetic anisotropy in Co(II) tetrahedral complexes, using a combined experimental and theoretical approach. From this work we propose a novel synthetic strategy for the synthesis of new generation SIMs.

For this study we focused our attention on unconventional exocyclic mesoionic ligands (Scheme S1). Mesoionic ligands are dipolar five- or six- membered heterocyclic compounds whose canonical resonance structures cannot be represented without any additional charges in them.¹⁰ To the best of our knowledge, however, their coordination chemistry has yet to be investigated. Such ligands offer flexibility allowing us to selectively change the coordinating substituents and thus we were able to probe the influence of the ligand donor atoms on the magnetic anisotropy.

The reaction of $\text{Co}(\text{II})\text{X}_2 \cdot 6\text{H}_2\text{O}$ (where $\text{X} = \text{Cl}$ or Br) with L_1 (where $\text{L}_1 = 2,3\text{-diphenyl-1,2,3,4-tetrazolium-5-olate}$) or with L_2 (where $\text{L}_2 = 2,3\text{-diphenyl-1,2,3,4-tetrazolium-5-thiolate}$) in methanol led to the isolation of blue (in case of L_1) or green (in case of L_2) single crystals when crystallized from acetonitrile.

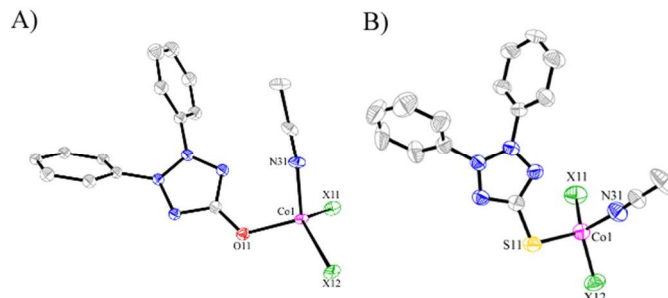


Fig 1. A) A representative thermal ellipsoid plot for complexes **1** and **2**, where $\text{X} = \text{Cl}$ (**1**) and $\text{X} = \text{Br}$ (**2**), B) A representative thermal ellipsoid plot for complexes **3** and **4**, where $\text{X} = \text{Cl}$ (**3**) and $\text{X} = \text{Br}$ (**4**); Hydrogen atoms are omitted for clarity.

The molecular structures were determined from single crystal X-ray diffraction, revealing mononuclear complexes of formula $[\text{Co}^{\text{II}}(\text{L}_1)(\text{X})_2(\text{MeCN})]$, where $\text{X} = \text{Cl}$ (**1**) or Br (**2**) and $[\text{Co}(\text{L}_2)(\text{X})_2(\text{MeCN})]$ where $\text{X} = \text{Cl}$ (**3**) or Br (**4**) (Figure 1 and Figure S1). Structural descriptions and related crystallographic parameters of the four complexes, **1** – **4**, are provided in the supplementary information (See Table S1–S4). Structurally there are no appreciable changes in the Co–X ($\text{X} = \text{Cl}$ or Br) and Co–N bond lengths (Table S3). Significant differences in the Co–S/O bond length is however observed; with longer S-atom bond distances of 2.3189 (**3**) and 2.3909 Å (**4**), compared to 1.957 (**1**) and 1.9475 Å (**2**) for the O donor mesoionic ligands.

Variable temperature (300 – 2 K) direct current (dc) magnetic susceptibility data were collected on polycrystalline samples of **1**–**4**, under an external magnetic field of 0.1 Tesla (Figure 2 and Figures S2 – S5). Room temperature $\chi_{\text{M}}T$ values of 2.83 (**1**), 2.82 (**2**), 2.81 (**3**) and 2.84 (**4**) $\text{cm}^3 \text{K mol}^{-1}$ are larger than the expected spin-only value of 1.875 $\text{cm}^3 \text{K mol}^{-1}$ ($S = 3/2$, $g = 2$) for a single tetrahedral Co^{II} ion.

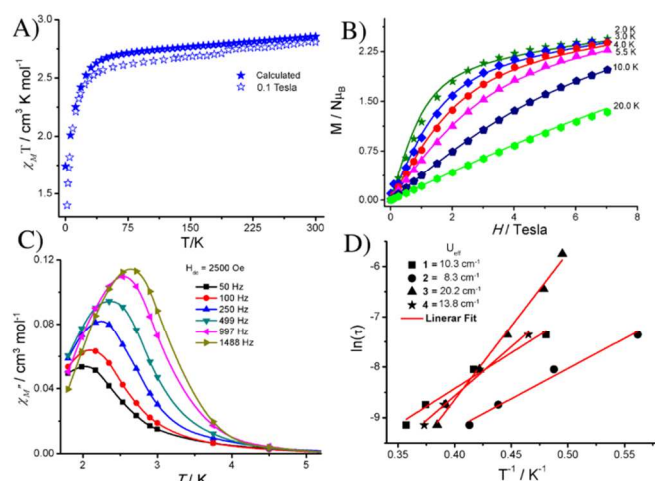


Fig 2. A) Temperature dependant $\chi_{\text{M}}T$ data recorded on polycrystalline sample of **3** open and filled stars represent the experimental data and the simulated $\chi_{\text{M}}T$ values using CASSCF+RASSI calculated parameters respectively. B) Field dependant magnetization data of **3** (symbols) measured at the indicated temperatures. The solid lines represent the simulated magnetization data using CASSCF+RASSI calculated parameters. C) Temperature dependant out-of-phase alternating current (ac) susceptibility measurement performed on polycrystalline sample of **3** between 1.8 K to 7.0 K at the indicated optimum external magnetic field. D) Arrhenius plot constructed from ac susceptibility measurement of all the four complexes (**1**–**4**).

Each complex displays temperature dependent behaviour as observed via a decrease in the $\chi_{\text{M}}T$ value as the temperature is reduced from RT to 50 K. This observation suggests that **1**–**4** possess a significant magnetic anisotropy. The influence of the anisotropy is even more pronounced below 50 K, resulting in a steeper decline of the $\chi_{\text{M}}T$ product, however, intermolecular antiferromagnetic interactions may also contribute to this behaviour. Isothermal magnetization data collected on polycrystalline samples of **1**–**4** at several temperatures (Figure S2–S5), reveal that the magnetization does not saturate at high fields, reaching values of $\sim 2.25 N\mu_{\text{B}}$ at 2 K. Furthermore the non-overlapping nature of the reduced magnetization plots confirms the presence of anisotropy/zfs (Figures S2–S5). In order to extract Spin Hamiltonian (SH) parameters, the $\chi_{\text{M}}T(T)$ and $M(H)$ data were simultaneously fitted using the PHI software package.¹¹ Best fits of the data yielded the following

parameters $\{S=3/2, g = 2.34, D = +15.61 \text{ cm}^{-1}\}$ (for **1**), $\{g = 2.34, D = +11.16 \text{ cm}^{-1}\}$ (for **2**), $\{g = 2.34, D = -11.30 \text{ cm}^{-1}\}$ (for **3**) and $\{g = 2.34, D = -10.32 \text{ cm}^{-1}\}$ (for **4**) (see Table 1, Table S5 and Figure S6 and the related discussion with respect to the sign of D , in the supplementary information).

In order to gain insight into the origin of the magnetic anisotropy of complexes **1** and **2**, we performed *ab initio* CASSCF+RASSI calculations (Tables S6 and S7). This method has been widely employed to compute the zfs parameters of several transition metal and lanthanide complexes.¹² The computed D values for complexes **1** and **2** are found to be $+20.35 \text{ cm}^{-1}$ and $+18.54 \text{ cm}^{-1}$ respectively (Table 1, Table S8 and Figure S7 for computed orientation of D tensor). Both the sign and the trend from the computed results agree well with the experimental fits, the magnitude however is overestimated.¹³ The simulated plots derived from the computed parameters reproduce both the experimental dc and magnetization data, adding further confidence to the extracted zfs parameters (Figures S2 and S3). Although the large positive D values determined for complexes **1** and **2** are encouraging, the sign is counterproductive towards the design of effective SIMs.

Table 1. CASSCF+RASSI^[b] computed D and E values, along with the g -values. The $\Delta E (^4A_2 \rightarrow ^4T_2)$ indicates the first excitation energy computed at the spin-free state of the Co^{II} complexes.

Complex	$D_{\text{fit}}^{[a]}$ (cm^{-1})	$D_{\text{cal}}^{[b]}$ (cm^{-1})	$ E/D _{\text{cal}}^{[b]}$ (cm^{-1})	$\Delta E^{[b]}$ (cm^{-1})	$g_{\text{xx}}, g_{\text{yy}}, g_{\text{zz}}^{[b]}$
1	15.61	20.35	0.177	2769.54	2.47, 2.39, 2.21
2	11.16	18.54	0.238	2644.26	2.49, 2.38, 2.23
3	-11.30	-15.90	0.197	2342.58	2.28, 2.36, 2.50
4	-10.32	-16.61	0.163	1966.356	2.31, 2.38, 2.54

[a] SH parameters extracted from PHI fit

A search of the Cambridge structural database (CSD) revealed a number of $\text{Co}(\text{II})$ tetrahedral complexes with np orbital (n is principal quantum number of group 15 and 16) containing ligands, where $n > 2$, which possess a negative zfs parameter (Table S9). In order to verify whether the diffuse orbitals play a role in modulating the sign of D , we replaced the oxygen atom in L_1 with sulphur or selenium atoms and proceeded with the structure optimization using the B3LYP/TZV setup (see ESI for computational details). The optimized structures and selected structural parameters are given in Table S10. These structures were then used for *ab initio* calculations to compute the SH parameters. Interestingly, it is predicted that the sign of D for both models are negative, with values of -20.46 cm^{-1} and -20.52 cm^{-1} for S and Se donors, respectively. It was based on these computational predictions that we synthesised complexes **3** and **4** which contain the sulphur (3p) donor ligand. (Table 1; See ESI for synthetic procedure and structural description. Also see Figure S7 and Table S8 for the computed orientation of the D tensor).

Due to the presence of a significant magnetic anisotropy, and with the prediction of an easy axis type anisotropy for **3** and **4**, alternating current (ac) susceptibility measurements were performed on **1**–**4**, to check for SIM behaviour (Figure S2–S5). No out-of-phase (χ_{M}'') susceptibility signals were observed using a 3.5 Oe oscillating ac field, under a zero external magnetic field. Upon application of a bias dc field of 0.25 T, **1**–**4** display frequency dependent χ_{M}'' signals, characteristic of a SIM. This implies unambiguously that each complex possesses significant anisotropy and QTM is likely to be the dominant mechanism for relaxation of the magnetization.¹⁴ From the frequency and temperature dependent data the effective energy barriers (U_{eff}) for the reorientation of magnetization are estimated to be 10.3 cm^{-1} ($\tau_0 = 7.68 \times 10^{-7} \text{ s}$), 8.2 cm^{-1} ($\tau_0 = 8.39 \times 10^{-7} \text{ s}$), 20.2 cm^{-1} ($\tau_0 = 1.49 \times 10^{-9} \text{ s}$) and 13.8 cm^{-1} ($\tau_0 = 8.12 \times 10^{-8} \text{ s}$) for **1**–**4** respectively (Figure 2 and Figures S2–S5). Interestingly, slow magnetic relaxation is observed for the $\text{Co}(\text{II})$ ions with non-uniaxial

anisotropy (**1** and **2**). A detailed rationale for this behaviour has recently been documented, revealing this can only be observed in the presence of a static magnetic field.¹⁵ The energy barrier observed for **3** is one of the largest reported for a Co(II) tetrahedral SIM and the field induced SIM behaviour exhibited by **3** and **4** are due to easy axis anisotropy (see EPR analysis below). Each isostructural complex reported displays significantly different energy barriers, implying a substantial change in the SH parameters, a trend which is clearly reflected in the computed values.

We performed preliminary EPR spectroscopy studies on all four complexes in order to experimentally observe the change of sign from easy plane anisotropy (+*D*) to easy axis anisotropy (-*D*) (Figure 3 and Figure S8). The spectra of **1** and **2** are similar, as are those of **3** and **4**, but both sets are markedly different from each other, implying a significant difference in the underlying electronic structure. The spectra of the oxo analogues (**1** and **2**) are straightforward, and are amenable to modelling only when *D* is constrained to be large (much larger than the energy of the microwave radiation being used) and, more importantly, positive: $g_{\text{iso}} = 2.4$, $D \gg 1.1 \text{ cm}^{-1}$, $E/D = 0.20$ (**1**); $g_{\text{iso}} = 2.4$, $D \gg 1.1 \text{ cm}^{-1}$, $E/D = 0.27$ (**2**). The spectra of **3** and **4** are not as straightforward, with not one but three features appearing at lower field. The most dominant of these features can be modelled with parameters consistent with a large negative *D*-value: $g_{\text{iso}} = 2.4$, $D \ll 1.1 \text{ cm}^{-1}$, $E/D = 0.28$ (**3**); $g_{\text{iso}} = 2.4$, $D \ll 1.1 \text{ cm}^{-1}$, $E/D = 0.28$ (**4**). In all cases, the simulations allowed for a small degree of orientation in the field. Although the large effective *g*-values observed in the thio complexes are consistent only with a negative *D*,¹⁶ the origin of the additional structure is not immediately apparent.

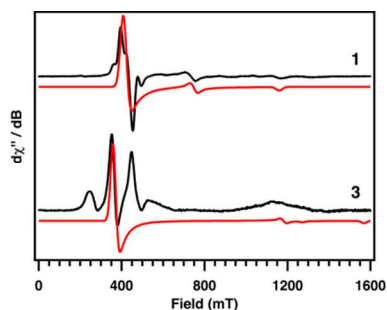


Fig 3. Q-band (34 GHz) EPR spectra of polycrystalline samples of **1** (top) and **3** (bottom) measured at 5 K. Red traces are simulations using the parameters given in the main text.

The crystal structure parameters of complex **3** agree well with the corresponding optimized model systems and the calculation performed on the X-ray structures of **3** and **4** yielded similar negative *D* values, in agreement with experimental evidence (Figure 2 and 3, Table 1, Tables S11 and S12). Since the sign of the zfs between O vs. S/Se donor atoms differ simply by replacing L_1 (in **1**) for L_2 (in **3**), we probed the reason for this switch. The magnetic anisotropy of tetrahedral Co(II) complexes which have no first-order orbital angular momentum is determined by a second order interaction between the electronic ground state and anisotropic excited states. This interaction is responsible for whether or not the sign of *D* is positive or negative. In general the transition between d-orbitals having the same $|m_l|$ values contribute to the D_{zz} component, leading to negative *D* values, while transitions between different $|m_l|$ values contribute to the D_{xx} and D_{yy} component of the anisotropy and thus enhances the positive value of *D*.¹⁷ To analyse these features in detail, the Eigen-value diagram for complexes **1** and **3** are plotted (see Figure 4). It is found that the $d_{x^2-y^2}$ and d_z^2 orbitals are found to be the lowest lying doubly occupied orbitals in both cases.

It is then found that the splitting of the d_{xz} , d_{yz} and d_{xy} orbitals differ drastically between complexes **1** and **3**. The d_{xy} orbital which interacts with the O/S atoms in a σ fashion is found to be destabilized in **1** and stabilized in **3** compared to the d_{xz}/d_{yz} orbitals, which are interacting with the chloride ligands. This is consistent with the X-ray structural parameters, where the Co-O bond length (1.957 Å) is found to be significantly shorter than the Co-S bond length (2.319 Å). Thus the lowest energy transition for complex **1** is predicted to be $d_{x^2-y^2} \rightarrow d_{yz}$, which predominantly contributes to the D_{xx} and D_{yy} terms, leading to a positive *D* value. On the other hand in complex **3** the $d_{x^2-y^2} \rightarrow d_{xy}$ is the lowest energy excitation which primarily contributes to the D_{zz} component (same m_l transitions) and this leads to a negative *D* parameter for this complex. The observed difference in the orbital ordering between **1** and **3** arises due to the difference in the metal-ligand interaction and the hard/soft nature of the ligands, with the Co-S bond being more covalent than Co-O bond.

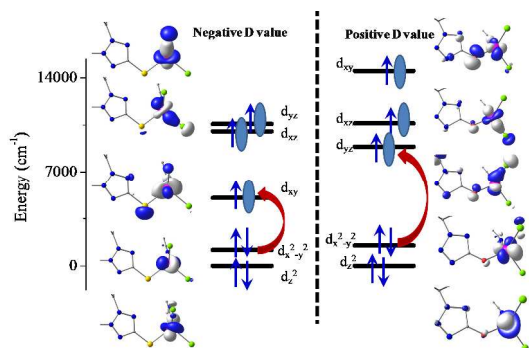


Fig 4. DFT computed Eigen value plots of the five d-orbitals for complex **3** (left panel) and **1** (right panel).

This is also reflected in the computed charges and the spin density values (Table S13). On a similar note the Co-Se model predicts a negative *D* value due to the soft nature of the ligand.¹⁸

The results presented in this article show that combined experimental, spectroscopic and computational methods reveal how to predict/switch the sign of *D* in Co(II) tetrahedral complexes. In order to generalize our prediction further, we have looked at different donor atoms, such as N and P (2p vs. 3p valence orbitals) containing ligands. The calculations were performed on crystal structures of reported complexes [CoBr₂(phenanthroline)] and [CoCl₂(PPh₃)₂], where the *D* values have been quantitatively determined by EPR spectroscopy.^{8c, 19} The calculated values are in agreement with their experimental findings [11.7 cm⁻¹ (experimental) vs 16.28 cm⁻¹ (computed)] and [-16.2 (experimental) cm⁻¹ vs -21.38 cm⁻¹ (computed)] respectively¹³ and follow the trend described in this article (Table S14). Further calculations performed on model complexes of [CoCl₂(PPh₃)(MeCN)] and [CoCl₂(py)(MeCN)] predict a negative (-41.13 cm⁻¹) and positive (+22.13 cm⁻¹) *D* value respectively (Table S15).

In summary, we have reported the single crystal X-ray structures of four isostructural Co(II) tetrahedral complexes (**1** - **4**) utilizing, for the first time, exocyclic mesoionic ligands. Detailed dc and ac magnetic susceptibility measurements reveal a significant anisotropy is present, with field induced SIM behaviour observed for all four complexes. Interestingly two of the four complexes (**3** and **4**) were synthesized based on computational predictions that they possess easy-axis type anisotropy. The switching of the magnetic anisotropy from easy plane to easy axis, by changing L_1 (hard donor) with L_2 (soft donor), was confirmed by EPR spectroscopy. To the best of our knowledge this is first time where predictions have been made and verified by parallel synthesis towards fine tuning the magnetic anisotropy. This works details a significant step forward towards the

design and synthesis of future SIMs. Further characterization of these complexes, and efforts to isolate other analogues are currently underway.

Notes and references

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Electronic Supplementary Information (ESI) available: The detailed experimental procedure for the ligand synthesis and all the metal complexes along with the dc and ac magnetic data plots including cif files are given in ESI. In addition the spin density plots and other theoretical calculations supporting evidences are also listed in ESI. CCDC numbers: 999464-999467. See DOI: 10.1039/c000000x/

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