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## Magnetic relaxation studies in trigonal bipyramidal cobalt(II) complexes

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Dedication to my supervisor Professor Talal Mallah on the occasion of his 60th birthday.

Abstract: We report the preparation and the full characterization of a novel mononuclear trigonal bipyramidal Coll complex [Co(NS<sub>3</sub><sup>iPr</sup>)Br](BPh<sub>4</sub>) (1) with the tetradentate sulphur containing ligand NS3<sup>iPr</sup> (N(CH2CH2SCH(CH3)2)3). The comparison of its magnetic behaviour with those of two previously reported compounds  $[Co(NS_3^{iPr})Cl](BPh_4)$  (2) and  $[Co(NS_3^{tBu})Br](ClO_4)$  (3)  $(NS_3^{tBu} =$  $N(CH_2CH_2SC(CH_3)_3)_3$  with similar structure shows that 1 displays a single-molecule magnet behaviour with the longest magnetic relaxation time (0.051 s) at T = 1.8 K, which is almost thirty times larger than that of 3 (0.0019 s) and more than three times larger than for  $\boldsymbol{2}$  (0.015 s), though its effective energy barrier (26  $\text{cm}^{-1})$  is smaller. 1, that contains two crystallographically independent molecules, presents smaller rhombic parameters (E = 1.45 and 0.59 cm<sup>-1</sup>) than 2  $(E = 2.05 \text{ and } 1.02 \text{ cm}^{-1})$  and 3  $(E = 2.00 \text{ and } 0.80 \text{ cm}^{-1})$  obtained from theoretical calculations. 2 and 3 have almost the same axial (D) and rhombic (E) parameter values, but present a large difference of their effective energy barrier and magnetic relaxation which may be attributed to the larger volume of BPh4<sup>-</sup> than CIO4<sup>-</sup> leading to larger diamagnetic dilution (weaker magnetic dipolar interaction) for 2 than for 3. The combination of these factors leads to a much slower magnetic relaxation for 1 than for the two other compounds.

#### Introduction

Single-molecule magnets (SMMs) that have been intensively studied for almost 30 year,<sup>[1]</sup> are envisioned to be employed for

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applications in (nano)spintronics, data storage and quantum computing due to their magnetic bistability.

The first studied SMM is  $[Mn^{III}_8Mn^{IV}_4O_{12}(O_2C_2H_3)_{16}(H_2O)_4]$ , commonly called Mn<sub>12</sub>(OAc),<sup>[2]</sup> that was first prepared by Lis et al. in 1980.<sup>[3]</sup> Thanks to its axial symmetry due to the presence of axially distorted Mn<sup>III</sup> ions, Mn<sub>12</sub>(OAc) has a large spin ground state (S = 10) with ground  $M_S$  = ±10 sub-levels responsible of its magnetic bistability.<sup>[1c, 1f]</sup> However, the control of the molecular symmetry and therefore magnetic anisotropy that is responsible for bistability is hard to achieve in polynuclear complexes. In recent years, research efforts shifted to design mononuclear SMMs where such a control is easier to reach and where magneto-structural correlation combining theory and experiment is accessible.<sup>[4]</sup> The success of such an approach allowed reporting large energy barriers and zero-field open magnetic hysteresis loops at high temperatures in Dy(III) containing complexes.<sup>[5],[6]</sup> Chemical control of the crystal field of d<sup>7</sup> transition metal ions in a linear Fe<sup>I</sup> complex, a linear Co<sup>II</sup> complex, a tetrahedral Co<sup>II</sup> complex, and trigonal bipyramidal Co<sup>II</sup> complexes led to slow relaxation of the magnetization and to an opening of the hysteresis loop at zero field, even above liquid helium temperature in some cases.[7]

Actually, if we want to employ SMMs for potential applications, mononuclear complexes are excellent candidates because they can be easily manipulated in solution and assembled on surfaces keeping their integrity, in particular when chelating ligands are used as for the complexes reported here.<sup>[7d]</sup>

Herein, we report the preparation and the full characterization of a mononuclear Co<sup>II</sup> complex [Co(NS<sub>3</sub><sup>IPr</sup>)Br](BPh<sub>4</sub>) (1) with NS<sub>3</sub><sup>IPr</sup> = N(CH<sub>2</sub>CH<sub>2</sub>SCH(CH<sub>3</sub>)<sub>2</sub>)<sub>3</sub> that adopts a trigonal bipyramid geometry thanks to the tetradentate NS<sub>3</sub><sup>IPr</sup> ligand. We compare its magnetic behaviour to those of two already reported complexes with the same geometry [Co(NS<sub>3</sub><sup>IPr</sup>)CI](BPh<sub>4</sub>) (2) and [Co(NS<sub>3</sub><sup>IBu</sup>)Br](ClO<sub>4</sub>) (3) with NS<sub>3</sub><sup>IBu</sup> = N(CH<sub>2</sub>CH<sub>2</sub>SC(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub>.<sup>[7d, 7f]</sup> Magnetic studies reveal that 1 exhibits an Ising-type anisotropy with the longest magnetic relaxation time (0.051 s at *T* = 1.8 K) despite its moderate effective energy barrier *U*<sub>eff</sub> = 26.2 cm<sup>-1</sup> and  $\tau_0 = 6.4 \times 10^{-9}$  s due to its inherent smaller transverse anisotropy and larger counter-ions diamagnetic dilution effect.

#### **Results and Discussion**

#### Syntheses

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ligand NS<sub>3</sub><sup>iPr</sup> and anhydrous cobalt(II) bromide with sodium tetraphenylborate (NaBPh<sub>4</sub>) in 1-BuOH afforded the trigonal bipyramidal topology compound **1**, the one positive charge is counter-balanced by a BPh<sub>4</sub><sup>-</sup> anion in the molecule (Scheme 1). It should be noted that in the final step of synthesis of NS<sub>3</sub><sup>iPr</sup>, 2-propanethiol is a poisonous gas with an obnoxious odour, all procedures must be carried out in an efficient fume hood. The apparatus must be connected to a series of washing bottles charged with an absorbing solution, such as chromic acid mixture or others.



Scheme 1. Synthesis procedure of ligand of NS<sub>3</sub><sup>iPr</sup> and compound 1.

#### **Description of the structures**

Compound **1** crystallized in the monoclinic space group  $P2_1/n$ , (Table S1). The cation structure comprised a central Co<sup>II</sup> ion surrounded by three sulphur atoms from ligand  $NS_3^{IPr}$  in the equatorial plane and a nitrogen atom from the ligand, with a bromide ion in the axial positions (Figure 1), the ligand adopts a

trigonal bipyramidal geometry with a pseudo-C<sub>3</sub> molecular symmetry axis. The compound has two crystallographically independent molecules (noted 1i and 1ii) in the asymmetric unit). The comparison of the structural bond lengths and angles of 1i and 1ii is shown in Table 1 together with those of compounds 2 and 3. For complex 1i, the Coll ion lies 0.375 Å (0.330 for 1ii) below the equatorial plane of the three sulphur atoms with an average SCoBr angle of 98.98° (97.90° for 1ii). The Co-N axial and Co-Br bond lengths are 2.351, 2.402 Å and 2.219, 2.400 Å for 1i and 1ii respectively. The average Co-S bond lengths, SCoS and  $\widehat{NCoS}$  angles are equal to 2.384, 117.62°, 81.04° and 2.388, 118.14°, 82.10° for complexes 1i and 1ii respectively. There are two main structural differences between 1i and 1ii: (i) the Co-Nax bond length is longer for **1i** and (ii) the deviation of the  $\widehat{SCoS}$  angle values in the equatorial plane from their average value is larger for 1i than for 1ii (Table 1). For the three compounds 1-3, all the different Co<sup>II</sup>-ligand bond lengths and angles will affect the zerofield splitting parameters and therefore their magnetic properties as analysed in the theoretical calculations part.



**Figure 1.** Molecular structure of compounds **1–3** obtained from X-ray diffraction. Violet sphere, Co; tan sphere, S; blue, N; brown, Br; green, Cl; black, C; snow, H. The most hydrogen atoms and counter-ion molecules were omitted.

Table 1. Relevant Co <sup>II</sup> –Ligand bond distances and a	angles and anisotropy	/ parameters for compound	s 1, 2 and 3
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	1 (this work)		<b>2</b> (ref 7d)		<b>3</b> (ref 7f)	
Complexes	i		i	ii	i	ii
<sup>a</sup> d <sub>CoN</sub>	2.351	2.219	2.263	2.408	2.231	2.274
<sup>a</sup> d <sub>CoS</sub>	2.384; 2.386; 2.382	2.384; 2.392; 2.389	2.412; 2.391; 2.388	2.362; 2.365; 2.378	2.435; 2.416; 2.385	2.412; 2.411; 2.407
<sup>a</sup> d <sub>CoX</sub>	2.402	2.400	2.255	2.265	2.361	2.383
<sup>a</sup> d <sub>Co-SSS</sub>	0.375	0.330	0.352	0.415	0.331	0.357
<sup>b</sup> SCoS	121.36; 118.15; 113.34	120.95; 117.15; 116.32	124.02; 122.08; 108.25	121.40; 116.35; 113.40	122.81; 122.28; 109.71	122.81; 116.83; 114.07
b,c SCoS	3.74; 0.53; -4.28	2.81; -0.99; -1.82	5.88; 3.94; -9.89	3.26; -1.79; -4.74	4.67; 4.14; -8.34	4.67; -1.31; -4.07
<sup>b</sup> SCoBr	100.05; 98.38; 98.50	98.18; 102.35; 93.18	103.49; 94.84; 95.86	103.82; 99.40; 96.98	93.85; 101.17; 98.19	98.66; 97.24; 99.29
<sup>b</sup> NCoBr	177.89	174.23	173.63	175.78	175.01	178.92
<sup>b</sup> NCoS	82.06; 80.39; 80.76	81.90; 82.68; 81.72	82.87; 81.94; 81.54	79.60; 81.29; 79.18	81.82; 83.31; 82.21	81.76; 81.69; 81.42
$^{d}U_{\mathrm{eff}}$	26.2		32.0		21.0	
$g_{exp}$	2.50		2.28		2.29	
$g_{calc}$	2.46		2.33		2.30	
$^{d}D_{exp}$	-20.0		-19.9		-20.2	
$^{d}D_{calc}(av)$	-15.8		-21.0		-19.8	
<sup>d</sup> D <sub>calc</sub>	-13.7	-17.9	-23.0	-19.1	-21.7	-18.0
<sup>d</sup> E <sub>calc</sub>	1.45	0.59	2.05	1.02	2.00	0.80

<sup>a</sup> In angstroms; <sup>b</sup> in degrees. <sup>c</sup> deviation of the SCoS angles from their average value; <sup>d</sup> in wavenumbers; (av) stands for average.

#### **Direct current magnetic studies**

Direct-current (dc) magnetic susceptibilities were measured on polycrystalline samples with a temperature range of 2–300 K (Figure S2). For 1,  $\chi_M T$  ( $\chi_M$  is the molar susceptibility) is constant between room temperature and 45 K with a value of 2.61 cm<sup>3</sup> K mol<sup>-1</sup> (Figure S2). Below 40 K, it decreases indicating the presence of zero-field (ZFS) splitting of the *S* = 3/2 manifold ( $M_s$  = ±1/2 and ±3/2 sublevels). The quality of the  $\chi_M T$  data in the high temperature range is not good enough because the relatively large amount of eicosane used during the measurement that generates a diamagnetic signal that has been corrected. We, therefore, focused on the analysis of the low temperature magnetization data where the diamagnetic contribution of eicosane is negligible. The magnetization (*M*) versus *B* plots at different temperatures (Figure 2) were fitted considering the following spin Hamiltonian and using a homemade software:

$$\widehat{H} = g\mu_{\rm B}\hat{S} \cdot \vec{B} + D\left[\hat{S}_z^2 - \frac{S_T(S_T + 1)}{3}\right] + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) \quad (1)$$

where  $S_T = 3/2$ ,  $\hat{S}$ ,  $\hat{S}_x$ ,  $\hat{S}_y$ ,  $\hat{S}_z$  are spin operators,  $\vec{B}$  is the applied dc magnetic field vector, g is Landé-factor that was assumed to be scalar,  $\mu_B$  is Bohr Magneton, D and E are the axial and rhombic ZFS parameters respectively.



**Figure 2.** Field dependent magnetization at variable temperatures for compound 1; ( $\bigcirc$ ) experimental data; (—) theoretical fit with the best *D* and *g* parameters; ( $\triangledown$ ) an average of the calculated magnetization considering *D* values from *ab initio* calculations.

The fit of the magnetization data gives the following values g = 2.51, D = -20.0 cm<sup>-1</sup> and E = 2.0 cm<sup>-1</sup>. Theoretical calculations give slightly smaller D (in absolute value) and E parameters for **1i** and **1ii** (Table 1). We calculated the magnetization curves from the theoretical parameters, made their average and obtained a reasonably good agreement with the experimental data but with a slightly different g value (2.46 instead of 2.51) (Figure 2). The theoretical energy barriers for the two independent molecules **1i** 

and **1ii** corresponding to the energy difference between the excited  $M_s = \pm 1/2$  and the ground  $M_s = \pm 3/2$  Kramers doublets calculated using the theoretical *D* values are equal to 28 and 36 cm<sup>-1</sup> (2|*D*|), while the fit of the magnetization data gives 40 cm<sup>-1</sup>. The main result here is that **1** similarly to the two reported compounds **2** and **3** has a negative ZFS axial parameter leading to the  $M_S = \pm 3/2$  sub-levels lying lower than the  $\pm 1/2$  ones, which is expected to lead to an Ising type anisotropy and a slow relaxation of the magnetization. Based on the ZFS parameters obtained from ab initio calculations (Table 1), we observe that compound **1** has the smallest axial ZFS parameter value.

#### Alternating-current magnetic studies

Ac susceptibility measurements were carried out on microcrystalline samples of compound 1 with an ac oscillatingdrive field of 3 Oe. We measured the ac susceptibility at T = 2 Kwith different frequencies and at variable applied dc magnetic field in order to find the optimum measurement dc field (Figures S3, S4) where the magnetic relaxation is slower. The optimal dc magnetic field is the one where the direct mechanism is minimized and quantum tunnelling of magnetization (QTM) is suppressed. In Figures S3, S4, we can hardly observe obvious out-of-phase susceptibility  $(\chi')$  under an applied zero dc magnetic field, however, upon increasing the dc magnetic field of 200 Oe, a maximum appears around 26.80 Hz, it shifts to low frequency when increasing the dc magnetic field up to 2600 Oe. At dc magnetic field of 1400 Oe, the maximum of the  $\chi^{"} = f(v)$  is around 4.31 Hz. If the dc magnetic field is further increased, the frequency of the maximum of the curve keeps constant till a value of 2600 Oe. The frequency variation of the maximum of  $\chi$ " vs. B (Figure S4) indicates that the optimal applied dc magnetic field is a range of 1400-2600 Oe, which also indicate the presence of QTM for the compound 1, and thus decreases the effective anisotropy barrier and speeds up the magnetic relaxation.



Figure 3. Frequency-dependent out-of-phase susceptibilities at 1.80 K with applied dc magnetic fields of 2000, 2000 and 3000 Oe for compounds 1, 2 and 3 respectively.

The ac susceptibility data were collected under an optimal field of 2000 Oe for compound 1 (Figures S13, S14), which revealed that 1 displayed frequency-dependence of the out-of-phase susceptibility and slow relaxation of magnetization. The comparison of the frequency-dependent out-of-phase signals at T = 1.8 K for compounds 1-3 (Figure 3) showed that the magnetic relaxation time for 1 is 0.051 s (Figure 3, calculated from experimental data and the same below), almost thirty times larger than for 3 (0.0019 s) and more than three times than for 2 (0.015 s), though the effective energy barrier of 1 (Figure 4 and Tables 1, 2) is smaller than 2, probably because 1 presents much smaller rhombic parameters E (1.453 and 0.589 cm<sup>-1</sup>) than 2 (2.055 and 1.021 cm<sup>-1</sup>) and 3 (2.00 and 0.80 cm<sup>-1</sup>, Table 1) as shown by theoretical calculations. In addition, we found that compounds 2 and 3 have almost the same Ising-type anisotropy parameter D values (D = -21.05 and -19.80 cm<sup>-1</sup>), but the effective energy barrier and magnetic relaxation of 2 are better than 3, though the rhombic parameter E value of 3 (Table 1) is a little smaller than 2, it should be due to the dilution effect (to some degree) of the counter-ions, because the volume of BPh4- is much larger than CIO4<sup>-</sup>. Furthermore, the relaxation time at 1.8 K of 1 (0.051 s) also presented much longer relaxation time than two popular trigonal bipyramidal complexes [Co(Me6tren)Cl]ClO4<sup>[7g]</sup> (0.0035 s) and [Co(TPMA)(CI)]CI<sup>[8]</sup> (0.016 s) at the same temperature.

The effective energy barrier ( $U_{eff}$ ) and relaxation time ( $\tau$ ,  $\tau_0$  is the relaxation time at infinite temperature) can be extracted by fitting the plot of  $\ln(\tau) vs. 1/T$  (Figure 4) of the high temperatures (namely Orbach relaxation) using Arrhenius equation  $\ln(\tau) = \ln(\tau_0) + U_{eff}/k_BT$ , which elicited a value of  $U_{eff} = 35.0$  K and  $\tau_0 = 1.2 \times 10^{-8}$  s for compound **1**. Meanwhile, we also attempted to fit the dependence of the relaxation time considering all relaxation processes with the following general expression:

$$\tau^{-1} = AH^4T + \frac{B_1}{1 + B_2H^2} + CT^n + \tau_0^{-1} \exp\left(-\frac{U_{eff}}{k_BT}\right)$$
(2)

where  $AH^4T$  ,  $\frac{B_1}{1+B_2H^2}$  ,  $CT^n$  and  $\tau_0^{-1} {\rm exp}\left(-\,U_{eff}/k_{\rm B}T\right)$  , corresponding to the direct, the QTM, the Raman and the Orbach processes respectively; A,  $B_1$ ,  $B_2$ , C, and n are coefficients, H is the applied dc magnetic field in Tesla, T is the temperature in Kelvin, Ueff is the thermal barrier of the Orbach relaxation mechanism in wavenumbers,  $\tau_0$  is the attempt time in seconds, and  $k_{\rm B}$  is the Boltzmann constant.<sup>[1k, 9]</sup> As shown in Figure 4, it is possible to obtain an excellent fit (Table 2, H = 0.2 T) with A =1200.5 s<sup>-1</sup> T<sup>-4</sup> K<sup>-1</sup>,  $B_1$  = 120650 s<sup>-1</sup>,  $B_2$  = 2.08 × 10<sup>6</sup> T<sup>-2</sup>, C = 1.12  $s^{-1}$  K<sup>-5</sup>, n = 5 (dimensionless),  $U_{eff} = 26.5$  cm<sup>-1</sup> (38.2 K) and  $\tau_0 =$  $6.4 \times 10^{-9}$  s, where the energy barrier is similar to the value obtained from Arrhenius linear fit (35.0 K). It should be mentioned that the parameters A,  $B_1$ , and  $B_2$  were obtained from the fit of the dependence of the relaxation time with the external applied dc magnetic field ( $\tau^{-1}$  vs B), we did this for all the three compounds 1-3 (Equation S1, Figure S3-S12). We also performed the fit of the dependence of the relaxation time only considering Orbach process and considering all relaxation processes in a similar way for compounds 2 and 3 to get their effective energy barriers (Figure 4, Table 2 and Table S3).

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**Figure 4.** Ln( $\tau$ ) as a function of 1/T from the data of Cole-Cole fitting. Blue line, Arrhenius fit according to the thermally activated region (Orbach process); red line, fit includes direct, QTM, Raman, and Orbach processes for compounds 1– 3, 2f, 2s represented the deconvoluted fast and slow relaxation of compound 2.

Table 2. Fit parameters for compounds 1–3. 2f, 2s represented the deconvoluted fast and slow relaxation of compound 2.

	1	2f	2s	3	
A / s <sup>-1</sup> T <sup>-2</sup> K <sup>-1</sup>	1.20 × 10 <sup>3</sup>	3.01 × 10 <sup>3</sup>	3.01 × 10 <sup>3</sup>	8.11 × 10 <sup>3</sup>	
<i>B</i> <sub>1</sub> / s <sup>-1</sup>	1.21 × 10⁵	1.10 × 10 <sup>3</sup>	1.10 × 10 <sup>3</sup>	2.00 × 10 <sup>4</sup>	
B <sub>2</sub> /T <sup>−2</sup>	2.08 × 10 <sup>6</sup>	1.20 × 104	1.20 × 10 <sup>4</sup>	4.60 × 10 <sup>2</sup>	
C / s <sup>-1</sup> K <sup>-n</sup>	1.12	0.5	17.0	4.10	
n	5	5	5	5	
<i>Н/</i> Т	0.2	0.2	0.2	0.3	
$\tau_0^{all}/s$	6.4 × 10 <sup>-9</sup>	1.5 × 10 <sup>-xxx</sup>	1.6 × 10 <sup>-11</sup>	2.9 × 10 <sup>-9</sup>	
$\tau_0^{\text{orbach}}/\text{s}$	1.2 × 10 <sup>−8</sup>	4.5 × 10 <sup>-9</sup>	6.4 × 10 <sup>-9</sup>	4.5 × 10 <sup>-8</sup>	
U <sub>eff</sub> <sup>all</sup> / cm <sup>-1</sup>	26.3	21.3	32.6	30.5	
$U_{\rm eff}^{\rm orbach}$ / cm <sup>-1</sup>	24.3	20.8	32.0	21.1	



Figure 5. Cole-Cole plot of compound 1 under an applied dc magnetic field of 2000 Oe, experimental data ( $\bigcirc$ ) and fit (—).

The ac data in the form of Cole-Cole plots for compound **1** (Figure 5) were fitted to the generalized Debye model<sup>[7d, 10]</sup> that allowed

extracting the relaxation times at different temperatures ( $\tau$ ) and their distribution ( $\alpha$ ) (Table S2).<sup>[11]</sup> The resulting  $\alpha$  values present with a range of 0.405–0.147 in the superparamagnetic distribution range for **1** (Table S2). The  $\alpha$  values increase up to 0.41 at 1.80 K and decrease to 0.15 and further approaching zero in high temperatures, which indicates the presence of a closely uniformly distributed relaxation process in the measured temperature range of 1.80–3.75 K.

#### **Theoretical Calculations**

In a trigonal bipyramid the splitting of the d orbitals by the ligand field leads to the scheme depicted in Figure 6 right, the  $d_{xy}$ ,  $d_{yz}$  orbitals have the lowest energy, the  $d_{xy}$ ,  $d_{x^2-y^2}$  orbitals have intermediate energies and the  $d_{z^2}$  one has the highest energy. All calculation results are reported in Tables 1 and S4. Our goal here is to perform a simple analysis of the relationships between the structure of the complexes and the anisotropy. From the theoretical results we will then seek to identify general ideas on the effect of the axial and equatorial ligands on the magnitude of the ZFS parameters.

Before performing the analysis of the relationship linking the energy difference between the states and the magnitude of the axial and rhombic zero-field splitting parameters, it is important to note that in  $C_{3v}$  symmetry (Figure 6) the first excited state  ${}^{4}A_{1}$  couples with the ground  ${}^{4}A_{2}$  state via the spin-orbit operator as we have already demonstrated[<sup>79, 12</sup>] and that was confirmed by others.<sup>[8, 13]</sup> This excited state brings a negative contribution to the overall *D* value because of its multideterminantal nature as we have already shown for Co<sup>II</sup> complexes in C<sub>3v</sub> symmetry and in particular for complexes **2** and **3**.<sup>[7f]</sup> While the  ${}^{4}E_{2}$  excited states contribute positively to *D*. It is, therefore, possible to analyse the magnitude of the overall *D* values of the different complexes by analysing the contributions coming from the excited  ${}^{4}A_{1}$  and  ${}^{4}E_{2}$  states via second order spin-orbit coupling (SOC).

The magnitude of |D| is inversely proportional to the energy difference between the ground and the excited states interacting through SOC at the second order of perturbations.<sup>[7d, 8, 14]</sup> For Co<sup>II</sup>  $(d^7, S = 3/2)$  ions in a trigonal bipyramidal environment with a symmetry close to  $C_{3\nu}^{[7g]}$  (Figure 6), the first excited quadruplet state (<sup>4</sup>A<sub>1</sub>) brings a negative contribution to D, while the <sup>4</sup>E state (splitted in the distorted geometry) brings a positive one; the excited <sup>4</sup>A<sub>2</sub> does not couple to the ground state by SOC.<sup>[12]</sup> The <sup>4</sup>A<sub>1</sub> state results from excitations involving the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xy}, d_{x^2-y^2}$  orbitals only and does not involve  $d_{z^2}$ . When including SOC this state interacts with the ground state through the  $l_z \cdot s_z$ part of the SO operator and therefore contributes negatively to D. On the contrary, the quadruplets coming from the splitting of the <sup>4</sup>E state involve mainly (but not only) the  $d_{z^2}$  orbital (Figure 6) and interacts with the ground state through the  $l_{+/-} s_{-/+}$  part of the operator that generates a positive contribution. In order to increase the negative contribution to D, the  ${}^{4}A_{1}$ - ${}^{4}A_{2}$  energy difference must decrease and the <sup>4</sup>E-<sup>4</sup>A<sub>2</sub> difference must increase (Figure 6 left, Table S4). This translates for the energy of the orbitals in a decrease of  $\Delta E_1$  and an increase of  $\Delta E_2$  (Figure 6 right) that can be made by longer equatorial Co-L distances and shorter axial Co–L bonds (larger axial  $\sigma$ -donating effect). The CoS<sub>eq</sub> and Co-Br bond distances in the coordination sphere of the two isomers are almost identical (Table 1). The main difference is the Co-N<sub>ax</sub> bond length that is larger for **1i** (2.351 Å) than for **1ii** (2.219 Å) leading to a smaller orbital energy separation ( $\Delta E_2$ ) between the  $d_{xy}$ ,  $d_{yz}$  and the  $d_{z^2}$  for the former than for the latter. The positive contribution to *D* is, therefore, larger for **1i** than for **1ii** leading to an overall less negative *D* value for **1i**. This is the origin of the difference of the axial ZFS parameter between **1i** and **1ii**.

The difference in the ZFS rhombic parameter values between 1i and 1ii can also be qualitatively rationalized. We have already carried out theoretical calculations on model complexes demonstrating that the more the SCoS angles deviates from their average values, the larger the rhombic term is.[7f] We can, therefore, analyse the contribution of the rhombic terms in light of our previous results. The presence of a rhombic parameter different from zero is mainly due to the distortion in the equatorial plane (deviation from the strict C<sub>3v</sub> symmetry) that induces the splitting of the <sup>4</sup>E excited state and concomitantly lift the degeneracy of the  $d_{xy}$ ,  $d_{x^2-y^2}$  orbitals. This splitting can be quantified by the deviation of the SCoS angles from their average values that is much larger for 1i than for 1ii (Table 1) and is, therefore, responsible for the largest rhombic E value for the former than for the latter. Indeed, the degree of splitting of the <sup>4</sup>E electronic term that is responsible for the magnitude of the rhombic parameter E is directly related to the distortion in the equatorial plane. The examination of this distortion for the isomers of the three compounds (Table S4) supports this correlation. Indeed, the largest deviation of the SCoS (9.89°) is found for isomer 2i where the energy splitting of the <sup>4</sup>E term is the largest (718.9 cm<sup>-1</sup>) leading to the largest *E* parameter (2.06 cm<sup>-1</sup>). While for **1ii**, the SCoS angle deviation of 2.8° leads to an energy splitting of 218 cm<sup>-1</sup> and to an *E* value of 0.59 cm<sup>-1</sup> (Table S4).



**Figure 6.** left, Calculated electronic energy (CASSCF) of the lowest quadruplets for complexes 1(i) and 1(ii); right, orbital energy diagram for a distorted trigonal bipyramidal Co(II) complex. The electronic states are labelled by the irreducible representation of the  $C_{3v}$  point group for simplicity even though the symmetry is lower due to distortion.

#### Conclusions

We prepared and fully characterized a novel sulphur-containing trigonal bipyramidal Co<sup>II</sup> compound **1** that behaves as a SMM

thanks to the trigonal pyramid environment imposed by the tetradente ligand that leads to a uniaxial ZFS and Ising-type anisotropy. Magnetic studies reveal that, despite a smaller energy barrier compound 1 has a magnetic relaxation time three times slower than that of 2. This was attributed to the difference in the rhombic parameters of the two compounds that was found to be correlated to the difference in the structural parameters. The much slower (thirty times) relaxation time of 1 compared to 3 is mainly due to the smaller energy barrier of 3, that may be due to two effects: the larger rhombic parameter and the smaller distance between the paramagnetic centres in 3 that may induce larger dipolar magnetic interactions. This last effect stems from the smaller size of  $CIO_4^{-}$  (3) compared to  $BPh_4^{-}$  (1). Therefore, in order to design Co<sup>II</sup> complexes with slow magnetic relaxation and large barrier to the reorientation of the magnetization one needs not only to perform a large axial anisotropy but also to decrease the rhombic term, preferably up to zero to eliminate the transverse process. Besides, large diamagnetic counter-ion(s), would increase diamagnetic dilution and slow the magnetic relaxation. It is important to note that other processes (Raman for example) involving molecular and lattice vibrations are active and contribute to speed up the relaxation process, but experimental determination of the vibrational modes are necessary to draw some qualitative conclusions on their effect.

#### **Experimental Section**

Generally, all starting materials were obtained commercially and were used without further purification unless otherwise stated. Elemental analyses for C, H, N were performed on a Thermo Scientific Flash analyser. Infrared (IR) spectra were recorded on a Bruker TENSOR-27 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) sample holder in a range of 4000–500 cm<sup>-1</sup>. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Aspect 300 NMR spectrometer. X-ray diffraction data were collected by using a Kappa X8 APPEX II Bruker diffractometer with graphite-monochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.71073 Å). Magnetic data were collected using a Quantum Design MPMS XL7 SQUID magnetometer.

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**Keywords:** magnetic anisotropy • magnetic relaxation • single molecule magnets • molecular magnetism

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### Entry for the Table of Contents

Layout 1:

## FULL PAPER

Counter anion together with subtle structural changes in coordination sphere slow down the magnetic relaxation time in trigonal bipyramidal Co(II) complexes.



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