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Structural Dependence of the Ising-type Magnetic Anisotropy and of the Relaxation Time in Mononuclear Trigonal Bipyramidal Co(II) Single Molecule Magnets

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S Supporting Information

ABSTRACT: This paper describes the correlation between Ising-type magnetic anisotropy and structure in trigonal bipyramidal Co(II) complexes. Three sulfur-containing trigonal bipyramidal Co(II) complexes were synthesized and characterized. It was shown that we can engineer the magnitude of the Ising anisotropy using ligand field theory arguments in conjunction with structural parameters. To prepare this series of compounds, we used, on the one hand, a tetradentate ligand containing three sulfur atoms and one amine (NS_3^{tBu}) and on the other hand three different axial ligands, namely, Cl⁻, Br⁻, and NCS⁻. The organic ligand imposes a trigonal bipyramidal arrangement with the three



sulfur atoms lying in the trigonal plane with long Co-S bond distances. The magnetic properties of the compounds were measured, and ab initio calculations were used to analyze the anisotropy parameters and perform magneto-structural correlations. We demonstrate that a smaller axial zero-field splitting parameter leads to slower relaxation time when the symmetry is strictly axial, while the presence of very weak rhombicity decreases the energy barrier and speeds the relaxation of the magnetization.

INTRODUCTION

Single molecule magnets $(SMMs)^{1-7}$ have been the focus of extensive research due to their potential as new materials for data storage and quantum computing.⁸⁻¹⁰ SMMs exhibit a slow relaxation of their magnetization that yields a magnetic hysteresis (i.e., bistability) at low temperatures (liquid-helium range) even in the absence of an external magnetic field.¹¹ This bistability is due to the existence of a degenerate ground state with two components of different magnetizations $(+M_{st} - M_{s})$ arising from the splitting of the M_s components of the ground spin state (S) by relativistic effects (mainly spin-orbit coupling). This property, which occurs in absence of an external magnetic field, is called zero-field splitting (ZFS). The magnitude and the nature (axial, rhombic, Ising, or planar) of the magnetic anisotropy account for the magnitude of the splitting, for the energetic ordering, and for the coupling (responsible for tunneling) of the M_s components. When the ground state has the largest M_s value, an easy axis of magnetization is present (D < 0), and when it has the lowest $M_{\rm s}$ value an easy plane of magnetization is present (D > 0). When D is negative, the energy difference between the largest and lowest $M_{\rm s}$ components (often referred to as an energy barrier) is proportional to the axial anisotropy parameter D, and

the coupling between the components are proportional to the rhombic parameter E.

The first generation of SMMs were polynuclear transition metal clusters that possessed a large spin (S) ground state in addition to a large Ising-type anisotropy (D).^{2,12} The classic example is the famous dodecametallic manganese-acetate family of SMMs ($Mn_{12}Ac$) that has S = 10 and energy barrier to the reorientation of their magnetization (U_{eff}) up to 74 K.^{2,12} The efforts, however, toward increasing the total spin of these kinds of systems has yielded a decrease in the total anisotropy of the clusters.¹³ For example, Brechin and Christou et al. reported a transition metal complex, which had a record barrier ($U_{\text{eff}} = 86$ K) but a |D| parameter of 0.62 K.^{14,15}

In the past decade, research efforts have focused on the synthesis of mononuclear SMMs with the idea that it is easier to control the structural requirements that lead to the anisotropy in these systems, and it is easier to manipulate these molecules in solution and on surfaces (a requirement for quantum information applications), even though some clusters (the Fe4 family) were perfectly stable in solution and successfully linked to surfaces.¹⁶ Slow relaxation was observed

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in many single lanthanide ion complexes,^{4,17-20} because they benefit from the large orbital angular momenta and large spinorbit coupling of the f-block elements. The f orbitals, however, are deeply buried in the valence shell rendering the control of the symmetry of the molecules difficult to predict in most cases.²¹ An alternative strategy is to construct mononuclear transition metal ion complexes that have the appropriate geometrical and chemical properties to display slow relaxation of the magnetization using the organic ligands to do so.^{22,23} Among few mononuclear complexes based on transition metal ions,²⁴⁻³² which display slow relaxation of the magnetization notable examples, include a tetrahedral Co(II) complex,^{24,32} trigonal bipyramidal Co(II) complexes, $^{26-28}$ and a linear Fe(II) complex.²⁵ A small opening of the magnetic hysteresis loop at zero direct-current field was first observed below 1 K,26 and recently at 2 K,33 for Co(II) complexes highlighting mononuclear transition metal ions as excellent SMMs.

Our group has previously studied trigonal bipyramidal symmetry around Co(II) and Ni(II) metal ions and showed that this geometry leads to Ising-type magnetic anisotropy (negative D values) that arises from the axial symmetry of the complexes imposed by the organic ligands.^{26,28,34} When the organic ligand imposes a given geometry to the complex, it is possible to develop a strategy to design complexes with predictable geometries and in some cases symmetries. Such design allows analyzing the origin of the magnetic anisotropy (nature and magnitude) in a first step and in a second step preparing molecules where anisotropy can be predicted. The asdesigned trigonal [Ni(Me6tren)Cl](ClO4) complex had an Ising-type anisotropy with a very large D value (close to -200 cm^{-1}),³⁴ and recently another Ni(II) trigonal complex was shown to possess even larger Ising-type anisotropy.³⁵ Replacing Ni(II) with Co(II) resulted in a complex that displayed slow relaxation of the magnetization and an opening of the hysteresis loop.²⁶ For the Co(II) complex, it was found that the ZFS parameter D changes when the Br⁻ is replaced by Cl⁻ (from -4.6 to -8.1 cm⁻¹, respectively). The differences in the magnitude of D were attributed to the σ/π effects of the ligands.²⁶ We could expand on these results and increase D by designing a molecule that has longer equatorial Co-L distances and shorter axial Co-L. By replacing the three nitrogen atoms of Me₆tren by sulfur atoms we considerably increased D to -23 $cm^{-1.2}$

The aim of this paper is to investigate structural and chemical effects on the magnitude of the magnetic anisotropy and the relaxation times in a series of three Co(II) compounds. We employed a sulfur-containing ligand (NS_3^{tBu}), which imposes a trigonal bipyramidal arrangement. We characterized their magnetic properties and analyzed two effects: (1) the influence of the Co–S bond distances and angles within each complex and among them and (2) the influence of the axial ligand (Cl⁻, Br⁻, or NCS⁻ and amine).

RESULTS AND DISCUSSION

Synthesis. The ligand NS_3^{tBu} was synthesized following a modified literature procedure.³⁶ The general synthesis of the complexes is as follows. To a solution of NS_3^{tBu} (1 equiv) in 1-butanol the anhydrous Co(II) salt was added (1 equiv) to yield a microcrystalline solid. Air-stable X-ray quality single crystals were obtained by slow evaporation of diethyl ether into a saturated ethanol/acetone (1/1) solution of the complex. The complexes were characterized further by Fourier transform

infrared (FT-IR) spectroscopy and electrospray ionization mass spectrometry (ESI-MS).

Structural Description. The structure of **2** was already reported.³⁷ We recorded a new set of data to have more accurate angles and bond distances necessary for calculations. As noted in Tables 1, S1, and S2, complexes **1** and **2** (Figures 1,

Table 1. Relevant Co(II)-Ligand Bond Distances and Angles and Anisotropy Parameters for Complexes 1, 2a, 2b, and 3

complex	1	2a	2b	3
space group	$P2_1/n$	Ρ.	$2_1/c$	$P2_{1}3$
$d_{Co-}X^{a}$	2.264	2.383	2.361	2.000
$d_{\text{Co-S}}^{a}$	2.404; 2.397; 2.389	2.412; 2.411; 2.407	2.435; 2.416; 2.385	2.380
$d_{\rm Co-S}({\rm av})^a$	2.397	2.410	2.412	2.380
$d_{\rm Co-N}^{a}$	2.287	2.274	2.231	2.345
SCoS ^b	118.88	116.83	122.81	117.58
	118.6	114.07	122.28	117.58
	116.56	122.81	109.71	117.58
Δ	2.18	7.36	12.835	0
g	2.29	2	.29	2.29
D_{exp}^{c}	-21.4		20.2	-11.0
$D_{\rm calc}^{\ c}$	-17.1	-18.0	-21.7	-13.8
$D_{\rm calc}({\rm av})^c$		-19.8		
$E_{\rm calc}^{c}$	0.24	0.80	2.00	0.00

^{*a*}In angstroms; (av) stands for average. ^{*b*}In degrees. ^{*c*}In inverse centimeters; (av) stands for average.



Figure 1. X-ray crystal structures of complexes 1, 2, and 3: Co = purple; C = gray; N = lilac; S = yellow; Cl = green; Br = brownorange; H = white; counterions were removed for clarity.

S1, and S2) crystallized in the monoclinic space group $P2_1/c_1$ while complex 3 (Figures 1 and S3) crystallized in the cubic space group $P2_13$. The cation structure in all complexes is comprised of a central Co(II) ion surrounded by three sulfur atoms in the equatorial sites, a nitrogen, and a chloride (1), bromide (2), or NCS (3) ion in the axial sites. As expected, the ligand imposes a trigonal bipyramidal arrangement in the three complexes with pseudo C_3 molecular symmetry axis for 1 and 2, while for 3, the complex has a strict three-fold symmetry $(C_{3\nu})$ point group) with equal equatorial Co–S bond distances, \widehat{SCoS} angles, and perfectly linear Naxial-Co-NCS atoms. We use here, for all complexes, the $C_{3\nu}$ point group notation for clarity even though the symmetry for the other complexes is lower. The bond distances for all compounds are reported in Table 1 and Table S1. Compound 2 has two crystallographically independent molecules in the asymmetric unit. The two molecules have almost the same average Co-S bond distances (2.410 and 2.412 Å), but the difference between the longest and shorter bond lengths is larger for one, noted 2a, (0.005 Å) than for the other, noted 2b, (0.05 Å; Tables 1 and S2). The Co-X bond distance ranges from 2.26 to \sim 2.38 for X = Cl and Br, but it is much shorter when X is NCS (2.00 Å). The Co N_{axial} bond distance is in the range of 2.287–2.345 Å and is the largest in 3.

Magnetic Properties. Direct-Current Magnetic Studies. The $\chi_M T$ is constant between room temperature and 50 K with values close to 2.4 cm³ K mol⁻¹ for 1 and 2 and 2.7 cm³ K mol⁻¹ for 3 (Figures S4–S6). Below 40 K the $\chi_M T$ decreases indicating magnetic anisotropy (ZFS of the $M_s = \pm 1/2$ and $= \pm 3/2$ sublevels), which was further confirmed by the magnetization (*M*) versus *B* plots (Figure 2). The *D* and *g*



Figure 2. Field-dependent magnetization at variable temperatures; (O) experimental data; (—) theoretical fit with the best *D* and *g* parameters; ($\mathbf{\nabla}$) average of the calculated magnetization considering *D* values from ab initio calculations for 1–3.

parameters are reported in Table 1, and they were obtained by fitting the data using the spin Hamiltonian $H = \beta \mathbf{S} \cdot \mathbf{g} \cdot B + D[\mathbf{S}_z^2 - S(S+1)/3] + E(\mathbf{S}_x^2 - \mathbf{S}_y^2)$ for S = 3/2, where **g** is a tensor, **S** are the spin operators, *B* is the magnetic induction, and *D* and *E* are the axial and rhombic anisotropy parameters, respectively. To avoid overparameterization, the rhombic term *E* was not considered in the fit procedures. The fit of the $\chi_M T$ data gives a rough value of the axial parameter *D* (Figures S4–S6) and allows determining the *g*-values for the three compounds that were subsequently used to fit the field-dependent magnetization.

It is important to stress here that because the Kramers nature of the levels (S = 3/2), the fit of the magnetization data is not unique, and a range of D and g values can give calculated data with reasonable agreement with experimental ones. The fit of the field-dependent magnetization data was performed by leaving free g_x (= g_y), g_z , and D (Table 1). It is worth noting that for 2, where two crystallographically independent molecules are present, we calculated the magnetization for each independent molecule using the D parameters obtained from ab initio calculations (see below), made their average, and compared with the experimental data (Figure 2); the average calculated curves are in excellent agreement with the experimental data. It is possible to include the parameter E in the fit procedure, but very good agreement between calculated and experimental values can be obtained with a large range of E values. The main result is that complexes 1 and 2 have D values close to -20 cm^{-1} , and 3 has an axial anisotropy that is about half in magnitude ($D = -11 \text{ cm}^{-1}$).

Alternating Current Magnetic Studies. To probe into the relaxation dynamics, we performed alternating current magnetic susceptibility measurements on microcrystalline samples of complexes 1, 2, and 3. The compounds showed frequency dependence of the out-of-phase susceptibility (Figures S7–S9) and slow relaxation of their magnetization. The alternating current data in the form of Cole–Cole plots (Figures S10–S12) were fitted to the generalized Debye model that allowed to extract the relaxation times at different temperatures (τ) and their distribution (α ; Table S3).³⁸ The comparison of the frequency-dependent out-of-phase signals at T = 1.8 K (Figure 3) for the three compounds shows that the relaxation time for 3



Figure 3. Experimental frequency dependence of χ'' at T = 1.8 with direct-current applied field = 3000, 3000, and 1600 Oe for 1 (red \bullet), **2** (blue \blacktriangle), and **3** (green \blacktriangledown), respectively; experimental data and fit (—).

is 1 order of magnitude larger than for 1 and 2 (0.01 vs 0.001 s). The $\ln(\tau) = f(1/T_B)$ plots, where T_B is the blocking temperature for a given frequency, are depicted in Figure 4. For 1 there is no clear linear part showing that the relaxation in the 1.8–4 K temperature range has little contribution from an Orbach process and that other processes dominate such as the direct and the multiphonon Raman-like ones.^{30,33,39} For 2, the situation is similar, but it is possible to fit the high-temperature



Figure 4. $\ln(\tau) = f(1/T_B)$ for 1 (red \bullet), 2 (blue \blacktriangle), and 3 (green \triangledown); experimental data and linear fit (—).

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data to the Arrhenius dependence of the relaxation time $\tau = \tau_0$ + exp (U_{eff}/kT) , where U_{eff} is effective barrier to the reorientation of the magnetization and τ_0 the relaxation time at infinite temperature. For 3, the fit of the data leads to $\tau_{02} = 2$ × 10⁻⁹ s and $U_{eff2} = 20 \text{ cm}^{-1}$ (Figure 4). The value of U_{eff} is the same for 2 and 3 (see Figure 4) despite the larger (in absolute value) *D* for the former than for the latter (-20.6 in comparison to -11.0). In addition, U_{eff} for 3 (20 cm⁻¹) is almost equal to 2lDl (22 cm⁻¹), while it is much weaker for 2 (21 cm⁻¹ instead of 41.2) considering the same temperature range for the two compounds. It is important to note that since there are only few figures to fit the linear dependence of $\ln(\tau)$, the extracted values of U_{eff} are only indicative. However, the difference between 3 and 2 has a physical meaning reflected in the difference of their relaxation time as seen in Figure 3.

Theoretical Calculations. Theoretical calculations were performed to rationalize the values of the ZFS parameters that were determined experimentally. As these parameters are very sensitive to the geometrical features, the theoretical study was performed using experimental geometries obtained from the Xray crystal data. Ab initio calculations were done using the twostep Complete Active Space Self Consistent Field (CASSCF) method followed by the spin-orbit state-interaction (SO-SI)⁴⁰ method implemented in the MOLCAS code.⁴¹ The averaged orbitals on 10 quadruplet states were optimized at the CAS(7,10)SCF level, and the wave functions used in the following analysis are the corresponding CASSCF ones. Calculations at the CASPT2 level were also performed.^{42,43} However, as can be seen in the Supporting Information (Figure S13), even if the spectrum presents exactly the same features as the CASSCF spectrum and would therefore support the same analysis, the values of D (Table S4) were not improved in comparison to those obtained at the CASSCF level. All information regarding the calculations are given in Supporting Information. The method of extraction of the parameters from both the effective Hamiltonian theory^{44,45} and the computed energies and wave functions has already been successfully used by our group for the determination of ZFS parameters.^{46–53} The energy of the four first excited states that bring the most important contributions to the ZFS parameters are depicted in Figure 5. The values of *D*, for all complexes, and their average for the crystallographically different molecules of compound 2 are reported in Table 1, and they are in good agreement with the values obtained from the fit of the experimental data.



Figure 5. CAS(7,10)SCF energies of the lowest quadruplet states calculated for compounds 1-3; 2a and 2b correspond to the two independent molecules of 2.

Structure/Magnetism Correlation. Several effects are analyzed: (i) the influence of the Co–S bond distances and angles within each complex and among them, (ii) the influence of the axial ligand (Cl, Br, or NCS), and (iii) the angular distortions around the Co(II) ion. As from perturbative arguments, we know that |D| is inversely proportional to the energy difference between the ground and the excited states;^{39,54–56} the energy of the various states is used to rationalize the nature and magnitude of the ZFS. Finally, as these energies can be related to those of the magnetic orbitals, magneto-structural correlations can be established from a ligand field analysis.

The main contribution to the anisotropy parameters is primarily due to the two quadruplet excited states, ${}^{4}A_{1}$ and ${}^{4}E$ (Figure 5). The first excited state ${}^{4}A_{1}$ is responsible for the negative value of *D*, while ${}^{4}E$ brings a positive but smaller contribution.^{26,27} Please note that there is another excited quadruplet state (${}^{4}A_{2}$ in light blue in Figure 5) just above the excited ${}^{4}A_{1}$ state but this state does not contribute to *D*. As complexes 1 and 2 do not have exactly a *C*₃ symmetry axis, the Co–S bond lengths and \widehat{SCoS} angles are different—there is a nonzero rhombic parameter *E*, which is due to the lift of degeneracy of the ${}^{4}E$ state (Figure 5). One may notice that *E* increases with the splitting.

The energy difference between the ground state ${}^{4}A_{2}$ and the first excited state ${}^{4}A_{1}$ can be related to the energy difference noted $\delta \varepsilon_{1}$ in Figure 6, between the two lowest molecular



Figure 6. (left to right) Orbital CAS(7,10)SCF energy diagram calculated for complexes **1**, **2a**, **2b**, and **3** and mean energy differences between the two lowest orbitals and the two first ones $(\delta \varepsilon_1)$ and between the two lowest ones and the highest one $(\delta \varepsilon_2)$. $\delta' \varepsilon_1$ is the energy difference between the first and the third orbital.

orbitals (MOs) (ϕ_1 and ϕ_2) and the two first excited ones (ϕ_3 and ϕ_4), because the state ${}^{4}A_1$ is obtained from a single excitation involving these sets of orbitals. As shown in Table 2, these orbitals are linear combinations of (d_{XZ} , d_{YZ}) and ($d_{X^2-Y^2}$, d_{XY}) orbitals, with larger coefficients on the d_{XZ} and d_{YZ} orbitals in the lowest MOs and larger coefficients on the $d_{X^2-Y^2}$ and d_{XY} in the highest ones. The coefficients of the most important determinants of the first excited state wave function are listed in Table 3, showing that this state is strongly multideterminantal. As predicted by group theory (in $C_{3\nu}$), the selection rule $\Gamma_{A_2} \otimes$ $\Gamma_{R_Z} \otimes \Gamma_{A_1} = \Gamma_{A_2} \otimes \Gamma_{A_2} \otimes \Gamma_{A_1} \supseteq \Gamma_1$ indicates that the $\hat{l}_Z \hat{s}_Z$ part of the spin-orbit operator couples the two states and that the contribution to *D* is negative, as ground and excited states have the same spin multiplicity.⁵³ The state ⁴E is also strongly

	CAS(7,10)SCF Orbitals on the 3d Atomic Orbitals of the Co(II) ^a	CAS(7,10)	of the Magnetic	2. Decomposition	Table 2
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complexes	1		2	a	21	b	3	5
AO	$d_{X^2 - Y^2}$	d _{XZ}	$d_{X^2-Y^2}$	d _{XZ}	$d_{X^2-Y^2}$	d _{XZ}	$d_{X^2 - Y^2}$	d_{XZ}
MO	d _{XY}	d_{YZ}	d_{XY}	d_{YZ}	d_{XY}	d_{YZ}	d_{XY}	d_{YZ}
$oldsymbol{\phi}_4$	72%	28%	78%	22%	82%	18%	78%	22%
ϕ_3	72%	28%	66%	34%	52%	48%	78%	22%
ϕ_2	27%	73%	32%	68%	47%	53%	22%	78%
ϕ_1	28%	72%	24%	76%	19%	81%	22%	78%

"As we do not have access to the overlap matrix, the squared coefficients were renormalized by their sum and multiplied by 100 to reach 100% of contribution. The reader may see the computed coefficients in Table S5. ϕ_5 is mainly spread over d_{Z^2} .

Table 3	. Weight o	f the D) omina	nt Determ	inants in	the	First
Excited	CAS(7,10)SCF S	States in	the Four	Molecul	es	

	_ _ ↑‡_ _ ↓ _ ↓ _	 	_ ↑ _₩ _+_₩	_ ↑ -₩+
1	0.446	0.400	.072	.053
2a	0.467	0.303	0.115	.0780
2b	0.675	0.248	0.032	0.04
3	0.289	0.289	0.197	0.197

multideterminantal.^{26,27} It results from excitations between the two previous sets of MOs $(\phi_1/\phi_2 \rightarrow \phi_3/\phi_4)$ and between the lowest MOs and the fifth one $(\phi_1/\phi_2 \rightarrow \phi_5$ essentially $d_{Z^3})$ orbital. Its energy difference with the ground state can therefore also be related to the energy difference noted $\delta \varepsilon_2$ in Figure 6. The selection rule $\Gamma_E \otimes \Gamma_{R_x,R_y} \otimes \Gamma_{A_1} = \Gamma_E \otimes \Gamma_E \otimes \Gamma_{A_1} \supseteq \Gamma_1$ here predicts that the $\hat{1}_+\hat{s}_- + \hat{1}_-\hat{s}_+$ part of the spin–orbit Hamiltonian now operates and that the contribution to *D* is positive. In summary, the ${}^4A_2 - {}^4A_1$ energy difference that brings a negative contribution to *D* is related to $\delta \varepsilon_1$, and the 4A_2 – 4E energy difference that brings a positive contribution to *D*

Let us start by analyzing the geometrical/chemical factors acting on the $\delta\varepsilon_1$ value (see Figure 6). Looking at the magnetic orbitals (the coefficients of these orbitals on the atomic ones are given in Table S5), one may see that there is an antibonding interaction between the sulfur orbitals and the Co ones mainly spread on $d_{X^2-Y^2}$ and d_{XY} . As a consequence, shorter Co–S bond lengths (see Table 1), that is, stroner equatorial σ donating effects, induce larger $\delta\varepsilon_1$ value.^{28,34} The Co–S distances decrease in the complexes ranging **2b**, **2a**, **1**, and **3**, as well as the *D* value in agreement with the increase of the $\delta\varepsilon_1$ value. As this contribution is the leading one, this argument rationalizes the *D* magnitude ordering in the four molecules.

One may note the singularity of the **2b** complex. Its first excited-state wave function has 0.675 weight (see Table 3) on a single determinant resulting from an excitation from ϕ_1 to ϕ_3 . As the energy difference between these two orbitals is much smaller ($\delta \varepsilon'_1$ in Figure 6) than $\delta \varepsilon_1$ in the other molecules, the energy of the first excited state of **2b** is particularly low (see Figure 5). Further analyzing the physical content of the orbitals given in Table 2, one may see that the weight of the d_{XY} and d_{X²-Y²} orbitals is much lower in orbital ϕ_3 in favor of d_{XZ} and d_{YZ} for that peculiar molecule. As the contribution of the former destabilizes this orbital, this effect is mainly responsible

for the low energy of ϕ_3 and therefore for the small value of $\delta \varepsilon'_1$. An extra effort of rationalization requires to go back to the geometrical structure. As the closure of the \widehat{NCoS} angles does not qualitatively vary between the complexes, this distortion cannot be invoked to rationalize the observed hybridization. On the contrary, looking at the \widehat{SCoS} angles in the equatorial plane one may see that one of them is 109°79′, that is, much smaller than the two others (122°). As shown in Supporting Information on model calculations, this angular distortion is responsible for the qualitative change in the orbital hybridization and for the further decrease of $\delta \varepsilon'_1$.

Let us now consider the factors acting on the $\delta \varepsilon_2$ energy difference and, in particular, the axial ligand effect. Looking at the magnetic orbitals, one may see that all ϕ_5 orbitals (mainly d_{Z^2}) orbitals have components on the axial ligand orbitals. In the spectrochemical series, Br⁻ exerts a weaker ligand field than Cl⁻ itself exerting a weaker ligand field than <u>NCS⁻</u>. From this argument, one may rationalize the decrease of the $\delta \varepsilon_2$ energy difference in the three molecules ranging 3, 1, and 2a. This effect is in favor of increasing positive contributions in complexes ranging 2, 1, and finally 3. Despite this, as the positive contribution to D of the ⁴E state is small (due to its high energy) this effect does not compensate the large negative contribution brought by the ${}^{4}A_{1}$ state, and the ordering of the D values is finally governed by the $\delta \varepsilon_1$ energy difference. Here again molecule **2b** shows a singularity: the $\delta \varepsilon_2$ value is particularly large, which is in favor of a smaller positive contribution to D. The analysis of the distances shows that this complex has smaller Co-N and Co-Br distances and therefore undergoes a stronger axial ligand field than the other molecules, which explains the larger $\delta \epsilon_2$ value. These results are corroborated by the larger coefficients of the magnetic orbitals ϕ_5 on the 2s and $2p_Z$ orbitals of the nitrogen (see Table S5). Finally one may also note that orbitals ϕ_1 and ϕ_3 of **2b** have significant weights on $4p_x$ and $4p_y$ of Br⁻; that is, the antibonding π -donor effect of Br⁻ in this molecule is stronger than in the others. In summary, in 2b there is a synergistic effect between weaker equatorial σ -donating effects and angular distortions that decrease $\delta \varepsilon_1$ and larger axial σ -donating effects that increases $\delta \epsilon_2$, both favoring a larger negative D value.

Concerning the rhombic parameter *E*, it decreases within the molecules ranging **2b**, **2a**, **1**, and **3**. This evolution can also be related to the variation of the \widehat{SCoS} angles (see Table 1) that renders asymmetrical *X* and *Y* in the equatorial plane. One may see that in all complexes, two angles are similar, while one is different. The deviation between the mean value of the former and the latter, spotted by the parameter Δ , exactly follows the evolution of *E*. Looking at the orbitals decomposition, one may see that this distortion causes a larger contribution of the d_{XZ} in one orbital of the first set (d_{YZ} in the other) and concomitantly

to a larger contribution of $d_{X^2-Y^2}$ in one orbital of the second set $(d_{XY}$ in the other) as corroborated by the coefficients of these orbitals in the magnetic ones (Table S5). Of course the fact that *E* is equal to zero for 3 is due to its $C_{3\nu}$ symmetry, in which *X* and *Y* are symmetrical.

CONCLUDING REMARKS

In conclusion we have shown the synthesis and characterization of three sulfur-containing trigonal bipyramidal Co(II) complexes. We show that it is possible to perform correlation between the geometrical structure of the complexes and the electronic structure of the ligands on the one hand and the magnitude of the magnetic anisotropy on the other hand. We demonstrate that, in the low-temperature range, the relaxation time of the complex with the weaker Ising type anisotropy is the slowest and that its energy barrier corresponds to what is expected if all other relaxation effects are absent. For the compounds with the weaker Ising type anisotropy parameters the relaxation is much faster. The main reason behind the "better" properties of complex 3 is the absence of the rhombic term due to the $C_{3\nu}$ symmetry point group that prevents tunneling between the low-lying $\pm 3/2$ sublevels, while the ground levels of the other complexes are made from mixtures of the $\pm 3/2$ and $\pm 1/2$ wave functions allowing a pathway for quantum tunneling. Therefore, to design Co(II) complexes with slow relaxation times and large barrier to the reorientation of the magnetization one needs not only to perform large Ising type anisotropy, but the rhombic term must be strictly equal to zero. For large axial anisotropy parameters to be obtained, the D_{2d} symmetry seems to be efficient as recently demonstrated,³³ but one must succeed to avoid small distortions that deviate from the strict symmetry, which is still a challenge.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.6b01966.

Crystallographic data (CCDC reference numbers 1448438, 1448439, and 1448440), magnetic data, and theoretical calculations (PDF)

X-ray crystallographic information (CIF)

X-ray crystallographic information (CIF)

X-ray crystallographic information (CIF)

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Notes

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