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Probing the Effects of Ligand Field and Coordination Geometry on Magnetic Anisotropy of Pentacoordinate Cobalt(II) Single-Ion Magnets

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Supporting Information

ABSTRACT: In this work, the effects of ligand field strength as well as the metal coordination geometry on magnetic anisotropy of pentacoordinated Co^{II} complexes have been investigated using a combined experimental and theoretical approach. For that, a strategic design and synthesis of three pentacoordinate Co^{II} complexes $[\text{Co}(\text{bbp})\text{Cl}_2] \cdot (\text{MeOH})$ (1), $[\text{Co}(\text{bbp})\text{Br}_2] \cdot (\text{MeOH})$ (2), and $[\text{Co}(\text{bbp})(\text{NCS})_2]$ (3) has been achieved by using the tridentate coordination environment of the ligand in conjunction with the accommodating terminal ligands (i.e., chloride, bromide, and thiocyanate). Detailed magnetic studies disclose the occurrence of slow magnetic relaxation behavior of Co^{II} centers with an easy-plane magnetic anisotropy. A quantitative estimation of ZFS



parameters has been successfully performed by density functional theory (DFT) calculations. Both the sign and magnitude of ZFS parameters are prophesied well by this DFT method. The theoretical results also reveal that the $\alpha \rightarrow \beta$ (SOMO–SOMO) excitation contributes almost entirely to the total ZFS values for all complexes. It is worth noting that the excitation pertaining to the most positive contribution to the ZFS parameter is the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation for complexes 1 and 2, whereas for complex 3 it is the $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation.

■ INTRODUCTION

Single-molecule magnets (SMMs) can show slow magnetic relaxation upon removal of an applied magnetic field.¹ The importance of these molecules lies in their potential applications in molecular spintronics and data storage.² Recently, significant attention has been paid to the molecular systems having only one metal center, considerable anisotropy, no intermetallic interactions, and magnetic properties related to SMMs, and these molecules are termed as single-ion magnets (SIMs). The interesting feature of single-ion magnets lies in the probable forecast of anisotropy established from ligand field theory. In parallel with the extensive study on lanthanide-based SIMs,³ substantial efforts have also been made to develop transition-metal-based SIMs.⁴ For all the reported 3d-SIMs, low-coordinated metal centers are commonly observed, where the anisotropy is enhanced because of the unrestricted orbital angular momentum.⁵ Among 3d-metal-based SIMs, Co^{II} compounds are generally of interest because of the noninteger spin ground state,^{6a} which decreases the possibility of quantum tunneling of magnetization (QTM).^{6b} Different from traditional SMMs where D is negative (D = axial ZFS parameter), a few mononuclear 3d-complexes have been reported as showing field-induced SMM behavior with a positive D value.^{4h,5b,c}

In this regard, for the control of the magnetic anisotropy of single-ion magnets, efforts have recently been increased.^{4m} Nevertheless, factors governing single-ion anisotropy are not well-studied, and control over magnetic anisotropy remains a challenging task. Ideally, the magnetic anisotropy and relaxation dynamics of mononuclear complexes can be tuned by controlling the ligand around the metal ion and its geometry, but a rational approach using combined experimental and theoretical studies is yet to be achieved. In this work, we have prepared a V-shaped ligand bbp [bbp = 2,6-bis(2benzimidazolyl)pyridine] with the anticipation that the rigid base of the ligand could favor a square pyramidal rather than trigonal bipyramidal geometry. To modulate the magnetic property, we chose thiocyanate ligands which may influence the geometry of the coordinated metal center. Herein, the dynamic magnetization study of three pentacoordinate Co^{II} complexes $[Co(bbp)Cl_2]$ ·(MeOH) (1), $[Co(bbp)Br_2]$ ·(MeOH) (2), and $[Co(bbp)(NCS)_2]$ (3) has been reported, and the combined effects of both terminal ligands and metal coordination

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geometry on the magnetic anisotropy have been investigated using a collective experimental and theoretical approach.

RESULTS AND DISCUSSION

Structural Description of 1–3. A single-crystal X-ray study revealed that **1–3** crystallize in the triclinic $P\overline{1}$ space groups (Table S1 in the Supporting Information). All complexes contain a mononuclear five-coordinate Co^{II} center (Figure 1). The X-ray crystal structure of complex 1 was reported previously,⁷ and only the lattice solvent molecule is different for the present case.



Figure 1. View of the molecular structures of complexes 1 (left) and 3 (right) emphasizing the square pyramidal and trigonal bipyramidal coordination geometries around Co^{II} centers, respectively. Color codes: Co (magenta), Cl (green), N (blue), S (yellow), C (gray).

Both complexes 1 and 2 are isostructural with each other, and the structure of 2 is presented in Figure S1. In complex 2, the Co^{II} center is coordinated by three nitrogen atoms from the bbp ligand, and two Br⁻ ions are located in the equatorial and axial positions. In complex 3, the Co^{II} center has trigonal bipyramidal coordination geometry where the Co^{II} center resides on the plane of the bbp ligand. There are three nitrogen atoms [one pyridyl (N3) and two thiocyanate groups (N6 and N7)] located in the equatorial plane, and N1 and N4 are placed at apical sites. The angles in the trigonal plane are close to the ideal value of 120° [N3–Co1–N7 = 134.07(6)°, N3–Co1–N6 = $116.37(6)^{\circ}$, and N6-Co1-N7 = $109.04(3)^{\circ}$]. However, the axial angle is considerably deviated from the ideal value $[180^\circ]$; $N1-Co1-N4 = 151.33(8)^{\circ}$; Tables S2 and S3]. The fivecoordinate Co^{II} centers assume geometries which are best defined as distorted square pyramidal and trigonal bipyramidal using SHAPE 2.1,8 with minimum continuous shape measure (CShM) values of 1.735, 2.163, and 2.146 for 1-3, respectively (Table S4). To analyze the distortion pathways, we have plotted the shape map for TBPY (trigonal bipyramid) compared to that for SPY (square pyramid). It can be observed from the shape map that complex 3 follows the interconversion path between the SPY and TPBY (Berry pseudorotation), but complex 1 (or 2) seems to be off this pathway and following another distortion pathway between a square pyramid and a vacant octahedron (VOC; umbrella distortion; Figure 2).

In all complexes, the mononuclear units are involved in intermolecular H-bonding with each other and also with interstitial solvent molecules (Tables S5 and S6). H-bonding interactions favor the construction of a supramolecular 2D-arrangement (Figures S2 and S3). Additionally, the $\pi \cdots \pi$ interactions are also observed between the phenyl rings of the benzimidazole groups with centroid-to-centroid distances of 3.754(2), 3.791(3), and 3.606(2) Å for 1–3, respectively. For an understanding of the packing arrangement, the Hirshfeld surfaces^{9a} and fingerprint plots^{9b,c} were constructed using CrystalExplorer 3.1.^{9d} A large, flat region appearing in the



Figure 2. Shape map for trigonal bipyramid (TBPY) and square pyramid (SPY) in complexes 1 and 3. The circles designate the locations of three ideal shapes labeled in boldface.

curvedness (front and back side) of complex **3** shows a significant overlap between two benzimidazole groups (Figure S4a–d). The 2D fingerprint plots were generated for complex **3** to explore the different types of contacts. In the 2D fingerprint plot, the wing region indicates the presence of the C…C contact (11.5%) involved in $\pi \dots \pi$ stacking present in the crystal packing for complex **3** (Figure S4e,f). Therefore, this study emphasizes the usefulness of Hirshfeld surface analysis and the quick observation of rare structural features^{9e} as well as supramolecular interactions.

Magnetic Property Studies. The phase purities of the assynthesized complexes were confirmed by the good agreements of powder X-ray diffraction patterns with the simulated ones (Figure S5). Magnetic susceptibility studies were carried out for 1–3 under a 0.1 T field. At 300 K, the $\chi_{\rm M}T$ values ($\chi_{\rm M}$ = molar magnetic susceptibility) of 2.57, 2.28, and 2.39 cm³ K mol⁻¹ were observed for 1-3, respectively, which are higher than the obtained spin-only value of 1.875 cm³ K mol⁻¹ for the high-spin Co^{II} center. These values are in the range 2.1–3.4 cm³ K mol⁻¹ for anisotropic Co^{II} centers.¹⁰ Upon the cooling of the complexes from room temperature, the $\chi_{\rm M}T$ values of 1-3 do not change down to 60 K, below which they suddenly fall, attaining values of 1.69, 1.46, and 1.52 cm³ K mol⁻¹, respectively, at 2 K (Figure 3 and Figure S6). The decline of $\chi_{\rm M}T$ values could be because of the inherent anisotropy of the Co^{II} centers. Reduced magnetization data attained the values of 2.3, 2.0, and 2.1 N μ_B (N μ_B = nuclear magneton) for 1–3, respectively, at 2 K and 7 T (Figure 3 and Figure S6). These values are lower than the theoretical saturation for an S = 3/2system ($M_{sat} = 3.3$ for g = 2.2) and do not saturate at a 7 T field, and it can be observed from Figures S6-S7 that all $M/N\mu_{\rm B}$ versus H/T plots do not merge with each other signifying anisotropic systems. A spin Hamiltonian has been used to describe the magnetic anisotropy qualitatively (eq 1):

$$H = g\mu_{\rm B}S \times B + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2)$$
(1)

where *D* and *E* represent the axial and rhombic terms of ZFS parameters. The PHI code¹¹ was used to estimate the ZFS values of Co^{II} by concurrent fitting of the $\chi_{\rm M}T$ versus *T* and *M*/ N $\mu_{\rm B}$ versus *H* plots. The best fit gave D = 14.5(2) cm⁻¹, E = 0, $g_x = 2.41$, $g_y = 2.25$, and $g_z = 2.01$ for 1; D = 8.4(7) cm⁻¹, E = 0, $g_x = 2.30$, $g_y = 2.20$, and $g_z = 1.99$ for 2; D = 10.7(4) cm⁻¹, $E = 1.1(2) \times 10^{-4}$ cm⁻¹, $g_x = 2.32$, $g_y = 2.23$, and $g_z = 1.99$ for 3.



Figure 3. $\chi_M T$ vs T plots measured at 0.1 T for complexes 1 (a) and 3 (b). $1/\chi_M$ vs T plots shown in the inset; $M/N\mu_B$ vs H plots for complexes 1 (c) and 3 (d) at the indicated temperatures. The red — are the best fit.



Figure 4. Frequency dependency of the in-phase (χ_{M}' , a and b) and out-of-phase (χ_{M}'' , c and d) ac magnetic susceptibility plots for complexes 1 and 3 under a 1000 Oe dc field.



Figure 5. Cole–Cole plots for complexes 1 (a) and 3 (b). The — represent the best fit. $\ln(1/\tau)$ vs 1/T plots for complexes 1 (c) and 3 (d). The red — are the best fit of the Arrhenius relationship.

The positive sign of the anisotropic parameter reveals the presence of a significant interaction between the excited and ground states by spin-orbit coupling (SOC). The D parameters of previously reported pentacoordinated CoII complexes have been shown in Table S7. It is clear that pentacoordinated high-spin CoII complexes with square pyramidal and trigonal bipyramidal geometries are systems of great interest for inducing strong magnetic anisotropy and can have different types of values of D parameters that varied from easy-axis- to easy-plane-type magnetic anisotropy. Both the sign and the magnitude of the ZFS parameters D's obtained for 1-3are found to be similar to those of the previously reported pentacoordinated Co^{II} complex [Co(TPMA)(CH₃CN)]-(BF₄)₂·CH₃CN (Table S7).^{5e} However, the studied complexes offer the opportunity to probe the influence of the ligand field strength as well as metal coordination geometry on their easyplane magnetic anisotropy.

For investigation of the relaxation dynamics of 1–3, ac susceptibility measurements were carried out in the temperature range 1.8–10 K, and the out-of-phase (χ_M ") signal was not detected under a zero dc field. However, all complexes exhibit temperature- and frequency-dependent ac signals under a 1000 Oe dc field (Figure 4 and Figures S8–S10). Also, the Cole–Cole plots (Figure 5 and Figure S10) were constructed from the frequency-dependent ac data. The fit of the $\chi_{M}^{"}$ versus $\chi_{\rm M}{}^{\prime}$ data by the generalized Debye model¹² produced the lphavalues (α parameter defines the width of the distribution of relaxation times; $\alpha = 1$ relates to an infinitely wide distribution, while $\alpha = 0$ signifies a relaxation with a single time constant) within the ranges 0.04–0.26 (1), 0.02–0.29 (2), and 0.08–0.31 (3). The effective energy barrier (U_{eff}) and relaxation times (τ_0) 's) were calculated using the Arrhenius equation¹³ $\ln(1/\tau) =$ $\ln(1/\tau_0) - U_{\text{eff}}/kT$. The best fit gave the following: $U_{\text{eff}} = 19.6$ K and $\tau_0 = 5.8 \times 10^{-5}$ s for 1; $U_{\rm eff} = 8.2$ K and $\tau_0 = 3.1 \times 10^{-5}$ s for 2; $U_{\rm eff}$ = 9.7 K and τ_0 = 4.6 × 10⁻⁵ s for 3 (Figure 5 and Figure S10). Recently, two types of mechanisms are proposed for the SMM behavior in 3d-SIMs with D > 0. The first type comes from the transverse anisotropy barrier proposed by Pardo et al.,^{4h} and the effective barrier is controlled by a substantial E value. This type is not relevant for these complexes, because experimental E values were found to be almost zero. The other type was suggested by Luis et al., and it was governed by the direct relaxation of the $M_{\rm S} = \pm 1/2$ states by the phonon bottleneck effect.¹⁴ Actually, these processes are repressed in a Kramers system with a substantial anisotropy regardless of the sign of the D parameter. For complexes 1-3, as the energy barriers obtained from ac susceptibility measurements are lower than the gap between the $M_{\rm S} = \pm 1/$

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Table 1. Experimental (D^{exptl}) and Calculated (D^{calc}) ZFS Parameters for Complexes 1–3 and Individual Excitation Contribution to the Total ZFS Parameter D

	$D_{\rm SOC}^{\rm calc}$ in cm ⁻¹						
complex	$\alpha ightarrow \alpha$	$\alpha \rightarrow \beta$	$\beta ightarrow \alpha$	$\beta ightarrow \beta$	$D_{ m SS}^{ m calc}$	total D^{calc} in cm^{-1}	D^{exptl} in cm^{-1}
1	-0.414	11.862	0.033	-0.665	0.272	11.09	14.5(2)
2	0.469	7.108	0.902	-1.059	0.361	7.79	8.4(7)
3	-0.141	9.002	-0.053	-0.299	-0.061	8.44	10.7(4)

2 and $M_{\rm S} = \pm 3/2$ states, the Orbach relaxation process is not applicable for the present case. Therefore, this supports the suggestion that quantum tunneling and Raman processes have contributed exclusively to the slow relaxation behavior of 1–3.

To gain more understanding of the origin of magnetization relaxation, the relaxation times were re-evaluated considering different relaxation processes. The experimental relaxation time has been examined starting from its field dependence at 2 K [Figure S11 (left)]. The first term in eq 2 exemplifies the QTM which is intensely affected by magnetic field; however, the second term (*C*) includes the weakly field-dependent processes (Raman, Orbach, etc.) and is therefore kept as constant, *C*, in eq 2.¹⁵ The relaxation time is well-described by this method (τ_{QTM} was calculated to be 1.82×10^{-4} s from eq 2), which confirms the significant role of the QTM of the ground state in the relaxation mechanism.

$$\tau^{-1} = B_1 / (1 + B_2 H^2) + C \tag{2}$$

At higher temperatures, Raman or Orbach should be the predominant process. The temperature dependence was examined at 0.1 T [Figure S11 (right)], including thermally active processes, which are either an Orbach process or follow a Raman mechanism.¹⁵ The experimental relaxation time is well-described by the method with a single power law, and values of n = 5.5, 4.6, and 4.2 are obtained for complexes 1–3, respectively ($\tau_{\rm QTM}$ was fixed at 1.82 × 10⁻⁴ s), which are close to the reported value by Colacio et al.¹⁶

$$\tau^{-1} = \tau_{\rm QTM}^{-1} + bT^n \tag{3}$$

Therefore, from the collective field and temperature dependence of the relaxation time, it can be concluded that QTM is the foremost pathway for the relaxation of the magnetization. However, the relaxation process is steered by an optical or acoustic Raman pathway that explains the thermal dependence.

Theoretical Calculations. To gain insight into the magnetic interaction at the molecular level, we have carried out density functional theory (DFT) studies of the magnetic anisotropy of complexes 1-3. The results for the DFT calculation of the D parameter are reported in Table 1. The comparison of the DFT results with the experimental data shows very good agreement. The four types of excitations which can be observed to contribute to the *D* tensor are $\alpha \rightarrow \beta$, $\beta \rightarrow \alpha, \beta \rightarrow \beta$, and $\alpha \rightarrow \alpha$. The different excitation contribution to the total ZFS reveals that it is the $\alpha \rightarrow \beta$ (SOMO–SOMO) excitation that contributes almost entirely to the total ZFS value. This information is in compliance with the fact that the SOC arises out of the mixing of the ground quartet and the excited doublet state. A close inspection of Table 1 also exposes a negligible spin-spin coupling (SSC) contribution toward the total ZFS parameter. A graphical depiction of 3d-orbitals and a molecular orbital (MO) diagram for all the complexes have been shown in Figures 6 and 7 and Figures S12-S14. The



Figure 6. Electronic configuration and d-orbital energy level diagram for complexes 1 (left) and 3 (right) from DFT calculations. Co—X bonds are placed along the *z* axis in 1 and 3, separately (X = Cl, NCS).

molecular orbital (MO) diagram along with the electron occupations for complex 1 are presented in Figure 6 (left) which shows that the three unpaired electrons reside in the d_{ru} d_{z}^{2} , and d_{x-y}^{2} orbitals. As is evident from the excitation contributions to SOC, the $\alpha \rightarrow \beta$ excitation corresponds to the $d_{xy} \rightarrow d_{x^2-y^2}^2$ excitation which renders the highest contribution to the ZFS parameter D. This is further established from the TDDFT (time-dependent DFT) difference density plot portraved in Figure 8 (left), where the cyan and the light purple surfaces represent electron-rich and electron-deficient areas (electron and hole densities), respectively. The apparent movement of electrons from the singly occupied d_{xy} orbital to the singly occupied $d_{x^2-y^2}$ orbital $(\alpha \rightarrow \beta)$ resulting in the excited doublet state unambiguously dictates that the mixing of the excited doublet state with the ground quartet state brings about the SOC-led ZFS parameter of the Co^{II} center. The MO diagram and corresponding difference density plot for complex 2 are presented in the Supporting Information (Figures S13 and S15). As expected, the electronic excitation picture is much the same as that for complex 1. A similar pictorial representation of the MOs for complex 3 is given in Figure 6 (right). It is worth noting from Figure 8 (right) that the excitation pertaining to the most positive contribution to the ZFS parameter is the $d_{z^2} \rightarrow d_{x^2-y^2}$ excitation. As the $\alpha \rightarrow \beta$ excitations take a major role in defining the ZFS parameter of complexes 1-3, the orbital splitting represented here confirms the positive ZFS parameter of these complexes. This fact conforms to the previous observation that such an excitation gives rise to the positive D value.^{41,m,5d}

It can be observed from the structural parameters of complexes 1 and 3 that changing the terminal ligand led to a change in the coordination geometry around the Co^{II} ion.



Figure 7. Graphical representation of the five 3d-orbitals of complex 1. Co-Cl bond is placed along the z axis in 1.



Figure 8. Charge transfer difference density plots for complexes 1 (left) and 3 (right), where light purple and cyan depict electrondeficient and electron-rich surfaces, respectively.

Thus, for understanding the effect of altering the ligand, a deeper insight from DFT is necessary. DFT calculations on all the geometries of complexes 1, 2, and 3 are performed with the respective Cl, Br, and NCS ligands replaced by point charges of magnitude -1.0.¹⁷ This calculation, on one hand, shows the effect of altering geometries on the ligand substitution as is performed experimentally in a very straightforward and convincing way, while, on the other hand, it also shows the effect of individual ligands, i.e., Cl, Br, and NCS, on the value of the ZFS parameter. We further denoted the point-charge-replaced geometries of complexes 1, 2, and 3 as complexes 1', 2', and 3', respectively. The *D* value for 1' is found to be 7.24 cm⁻¹ while for complex 1 it is 11.09 cm⁻¹ (Table 2). Thus, it is

Table 2. Values of the Total ZFS Parameter (D) after Replacement of the Terminal Ligands with Point Charges of the Same Magnitude for Complexes 1-3

сс	omplex	$\alpha \rightarrow \beta$ excitation (cm ⁻¹)	total D (cm ⁻¹)
	1	11.86	11.09
	2	7.11	7.79
	3	9.00	8.44
	1′	8.78	7.24
	2'	-8.54	-6.95
	3′	6.22	9.23

apparent from the comparison of *D* values, for the same geometry of complex 1 in the presence and absence of Cl as the ligand, that Cl induces a positive contribution to the total *D*. It is also noted that the major contribution (8.78 cm⁻¹) in 1' comes from the $\alpha \rightarrow \beta$ excitation which is in parity with complex 1. The similar calculation for the geometry of complex 3 manifests a negative contribution of the NCS ligand toward the total *D* value. Complex 3' has a ZFS parameter value of 9.23 cm⁻¹, while the same geometry with the ligand NCS instead of the point charge, i.e., complex 3, revealed a *D* value of 8.44 cm⁻¹ (vide supra). A major contribution of the individual $\alpha \rightarrow \beta$ excitation is 6.22 cm⁻¹ in the case of complex

3' (Table 2). For the pair 2 and 2', also, the major contribution arises from the $\alpha \rightarrow \beta$ excitation akin to those of complexes 1 and 3. Hence, the above numerical experiment clarifies the effect of both geometry and ligand field toward the ZFS in the synthesized complexes. A more precise analysis of the results from the point-charge computations exposes that the lack of π bonding is the foremost reason behind the change in the D value of complexes 1 and 2. From the orbital diagrams, it is clear that the d_{xy} orbital has a large π -type contribution from the Cl ligands, and the change in D seems to arise from the lack of π -character of the Co–Cl bond in complex 1. The effect of π -donation in the ZFS parameter is further fortified from the example of complex 2. Thus, a good π -donor should generally be capable of introducing a more positive contribution toward the ZFS parameter of the molecule. This is similar for complex 3, for which the same analysis suggests that a good π -acceptor will have a negative contribution toward the total D of the molecule.

We have also performed ab initio calculations with CASPT2 methodology. This calculation was done with the ANO-RCC basis set in the MOLCAS7.8 suite of software,^{18a} and the *D* values were found to be -13.06, -3.65, and -44.31 cm⁻¹ for complexes 1, 2, and 3, respectively. Thus, compared to the experimental results, the CASPT2 method is found to give a poor prediction of the sign and magnitude of the ZFS parameters. We have also calculated the ZFS parameter using the NEVPT2 formalism implemented in ORCA. The *D* values computed using this method are found to be 41.13, 42.73, and 35.97 cm⁻¹ for complexes 1, 2, and 3, respectively (Table S8). Thus, the results are also in disagreement with the experimental results. Therefore, the DFT calculations on these complexes are in better agreement with the experimental results. Previous reports have also shown that DFT can calculate ZFS parameters for Co^{II} complexes.^{17,18b-e}

It was reported that structural changes around the coordination environment can modulate the magnetic anisotropy and relaxation behaviors of the resulting complexes.¹⁹ However, the present series of mononuclear Co^{II} complexes 1-3 reveals only a minor effect of the geometry and the terminal ligand field on the magnitude of the magnetic anisotropy parameter *D*. We assume that this is because of the stronger ligand field effect of the benzimidazolylpyridine. Thus, the little variances in the magnetic properties of complexes 1-3 come from two combined influences; the first one is the difference in the ligand field strength imposed by the terminal ligands, and the second one is the slight changes of the metal coordination geometry.

In conclusion, it is conceivable to stipulate the coordination geometry around the Co^{II} center by using the 2,6-bis(2-

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benzimidazolyl)pyridine ligand in conjunction with the terminal ligands. The present results demonstrate the slight change in the magnetic anisotropy of pentacoordinate Co^{II} SIMs by structural modification. Hence, propagation of the present study is anticipated to explore interesting routes for magnetochemists to determine ZFS parameters in low-coordinate complexes.

EXPERIMENTAL SECTION

Materials and General Procedure. Magnetic studies were done using a Quantum Design SQUID-VSM magnetometer. The obtained values were amended for the experimentally measured contribution of the sample holder, whereas the derived susceptibilities were corrected for the diamagnetic contribution of the sample, assessed from Pascal's tables.²⁰ Elemental analysis was performed on an Elementar Microvario Cube elemental analyzer. The IR spectrum was measured on KBr pellets with a PerkinElmer spectrometer. Powder X-ray diffraction (PXRD) data was measured on a PANalytical EMPYREAN instrument using Cu K α radiation.

Crystal Data Collection and Structure Determination. Intensity data were measured on a Brüker APEX-II CCD diffractometer by graphite monochromated Mo K α radiation (α = 0.710 73 Å) at 140, 120, and 296 K for complexes 1-3, respectively. Data collection was done using φ and ω scan. The structure was solved by direct methods followed by full matrix least-squares refinements using SHELXTL.²¹ After that, difference Fourier synthesis and least-squares refinement exposed the positions of the remaining non-hydrogen atoms. Determinations of the crystal structure, orientation matrix, and cell dimensions were made following reported methods. Lorentz polarization and a multiscan absorption correction were incorporated. Non-hydrogen atoms were refined with anisotropic displacement, and H atoms were located geometrically and polished by riding model. All calculations were performed by SHELXL 97, PLATON 99,²³ and WinGX systemVer-1.64.²⁴ Crystallographic data for complexes 1-3 have been given in Table S1.

Computational Details. The DFT computations were done with the help of the ORCA package.²⁵ The *D* parameter was calculated using the TPSSH functional and TZV basis set in the unrestricted Kohn–Sham framework. An auxiliary TZV/J Coulomb fitting basis set was used during the calculation. The estimation of the SOC effects was performed using the mean-field approximation (SOMF) incorporating the spin–own-orbit as well as spin–other-orbit interactions in the exchange term. The computation of the ZFS parameter was performed through the popular coupled perturbed (CP-SOC) technique developed by Frank Neese which is known to produce results that are more realistic compared to those of any other method.²⁶ We have also used the zero-order regular approximation (ZORA) for relativistic corrections in all the computations.

Synthesis of Ligand bbp. A 3.34 g (19.8 mmol) portion of pyridine-2,6-dicarboxylic acid and 4.68 g (43.7 mmol) of 1,2-phenylenediamine were mixed with 155 g of polyphosphoric acid under N₂ atmosphere. This was heated at 220 °C for 5 h, and was then cooled to 140 °C and added into 1 L of H₂O. The resulting blue precipitate was collected by filtration, dispersed in 500 cm³ of 10% Na₂CO₃(aq), and further stirred for 30 min. Then, the mixture was filtered and dispersed in cold H₂O (800 cm³). The pH of the solution was adjusted to 4 by 10% HCl(aq) and recrystallized from MeOH. The ligand was found as a pure white crystal of 72% yield (4.5 g). Selected IR data (KBr pellet, 4000–400 cm⁻¹) ν/cm^{-1} : 3185 (ν_{N-H}), 1600 (ν_{C-C}), 1573 ($\nu_{C=N}$), 1460 (ν_{C-N}), 1278 (ν_{C-N}).

Synthesis of Complex 1. Both ligands bbp (31 mg, 0.1 mmol) and CoCl₂·6H₂O (23 mg, 0.1 mmol) were dissolved in 10 mL of MeOH, and the mixture was stirred at room temperature for 4 h. The resulting mixture forms a deep green solution which was filtered and kept for slow evaporation that yields green crystals of $[Co(bbp)Cl_2]$ ·(MeOH) (1) after 3 days. The crystals were washed with Et₂O and airdried: yield (80%). Anal. Calcd for C₂₀H₁₇CoN₅OCl₂: C, 50.76; H, 3.62; N, 14.80%. Found: C, 50.89; H, 3.71; N, 14.86%. Selected IR

data (KBr pellet, 4000–400 cm⁻¹) ν /cm⁻¹: 3187 (ν _{N-H}), 1610 (ν _{C-C}), 1566 (ν _{C=N}), 1460 (ν _{C-N}), 1272 (ν _{C-N}).

Synthesis of Complex 2. Both the ligand bbp (31 mg, 0.1 mmol) and CoBr₂ (22 mg, 0.1 mmol) were dissolved in 10 mL of MeOH, and the mixture was stirred at room temperature for 3 h. The resulting mixture forms a deep green solution, and that was filtered and kept for slow evaporation that yields green crystals of [Co(bbp)Br₂] (MeOH) (2) after 4 days. The crystals were washed with Et₂O and air-dried: yield (74%). Anal. Calcd for C₂₀H₁₇CoN₅OBr₂: C, 42.71; H, 3.05; N, 12.46%. Found: C, 42.81; H, 3.13; N, 12.40%. Selected IR data (KBr pellet, 4000–400 cm⁻¹) ν/cm^{-1} : 3186 (ν_{N-H}), 1612 (ν_{C-C}), 1565 ($\nu_{C=N}$), 1458 (ν_{C-N}), 1270 (ν_{C-N}).

Synthesis of Complex 3. Both the ligand bbp (31 mg, 0.1 mmol) and Co(ClO₄)₂·6H₂O (36 mg, 0.1 mmol) were dissolved in 10 mL of MeOH, and KSCN (20 mg, 0.2 mmol) dissolved in H₂O (10 mL) was added to the previous solution. The resulting mixture forms a deep brown solution and was further stirred at room temperature for 6 h. The green precipitate was filtered and recrystallized from a MeOH/ MeCN mixture (1:1), which yields green crystals of [Co(bbp)-(NCS)₂] (3) after 4 days. The crystals were washed with Et₂O and airdired: yield (61%). Anal. Calcd for C₂₁H₁₃CoN₇S₂: C, 51.87; H, 2.69; N, 20.16%. Found: C, 51.98; H, 2.57; N, 20.23%. Selected IR data (KBr pellet, 4000–400 cm⁻¹) ν/cm^{-1} : 3188 (ν_{N-H}), 2049 (ν_{NCS}), 1607 (ν_{C-C}), 1569 ($\nu_{C=N}$), 1458 (ν_{C-N}), 1275 (ν_{C-N}).

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.7b00233.

Theoretical background, analysis parameters, figures of 1-3 structures, bond distances and angles, and PXRD and magnetic characterizations (PDF)

Accession Codes

CCDC 1437903–1437904 and 1538781 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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