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Slow Magnetic Relaxation in a One-Dimensional Coordination Polymer Constructed from Hepta-Coordinate Cobalt(II) Nodes

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Abstract: A one-dimensional coordination polymer was synthesized employing hepta-coordinate Co^{II} as nodes and dicyanamide as linkers. Detailed direct current (DC) and alternating current (AC) magnetic susceptibility measurements reveal the presence of field-induced slow magnetic relaxation behavior of the magnetically isolated seven-coordinate Co^{II} center with an easy-plane magnetic anisotropy. Detailed ab initio calculations were performed to understand the magnetic relaxation processes. To our knowledge, the reported complex represents the first example of slow magnetic relaxation in a one-dimensional coordination polymer constructed from hepta-coordinate Co^{II} nodes and dicyanamide linkers.

Keywords: Cobalt(II); coordination polymer; single ion anisotropy; slow magnetic relaxation

1. Introduction

In the past few decades, the design and synthesis of coordination polymers (CPs) have attracted significant attention because of their different structural dimensionalities (1D, 2D and 3D), interesting topologies and potential applications [1–4]. The metal ions in CPs are the source of some interesting physical properties including magnetism apart from their structural role. In recent years, rapid developments in the field of single molecule magnets (SMMs) have been observed because of their applications in data storage, quantum computing, and spintronic [5–7]. The smallest possible SMMs are known as single ion magnets (SIMs), where slow magnetic relaxation occurs from a single metal center [8]. The most interesting feature of single ion magnets (SIMs) lies in the possible tuning of their magnetic anisotropy through the regulation of the coordination number and ligand field. Along with the lanthanides-based SIMs [9–14], there has been significant research interest in transition metal-based SIMs [15–37]. In the family of 3D-SIMs, Co^{II} -based complexes draw significant attention because of their non-integer spin ground state, which decreases the probability of quantum tunneling of magnetization (QTM) [38]. Most of the Co^{II} -based SIMs reported so far concern mononuclear complexes and less interest has been given for making Co^{II} -containing CPs. In 2014, Andruh et al. first reported two Co^{II} -based 2D CPs using linear and angular ligands simultaneously where the well-separated six-coordinated Co^{II} centers behave as SIMs [39]. In 2015, Gao et al. also reported a one-dimensional Co^{II} CP in which the independently six-coordinated Co^{II} ions feature SIM behaviour [40]. The abovementioned examples were based on magnetically separated octahedral Co^{II} ions, but less attention has been given to prepare hepta-coordinate Co^{II} centers as building blocks for the construction of 1D Co^{II} -based single-ion-magnet. In recent times, it has been observed that the hepta-coordinate Co^{II} SIMs are very attractive candidates due to their large magnetic anisotropy [41–50].

Furthermore, these systems can serve as excellent building blocks for the preparation of larger clusters due to the labile axial ligands. Huang et al. reported the first example of field induced SIM behavior of pentagonal-bipyramidal Co^{II} complex [42]. The positive sign of *D* parameter was verified by experimentally and theoretically [41–47] and further confirmed by high-field electron paramagnetic resonance (HFEPFR) [49]. In the case of a pentagonal-bipyramidal Co^{II} system, the spin-orbit coupling between ground electronic states with two excited electronic states results in the easy plane magnetic anisotropy. Therefore, significant efforts have been made in order to modulate the easy plane magnetic anisotropy by modulation of the coordination environment of various pentagonal-bipyramidal Co^{II} complexes [43,45]. In our earlier report on pentagonal-bipyramidal Co^{II} complexes [41], we showed that either by employing a better σ donor axial ligand or by using a symmetric equatorial ligand, it is possible to decrease the magnitude of the *D* parameters as well as the energy barrier. Both experimental and ab initio calculations disclosed that the sign of the *D* parameter is generally unaffected by the change in coordination environments, whereas the appropriate weak σ -donor axial ligand can be able to considerably increase the magnitude of the *D* parameter in pentagonal-bipyramidal Co^{II} complex [41].

Inspired by the aforementioned consideration, we prepared a Co^{II}-based 1D coordination polymer, [Co(H₃daps)(dca)]·(MeOH)₂·(MeCN) (**1**, where H₄daps = 2,6-bis(1-salicyloylhydrazonoethyl) pyridine and dca = dicyanamide) employing hepta-coordinate Co^{II} as nodes and dicyanamide as linkers in which the well-separated seven-coordinated Co^{II} centers behave as SIMs. The magnetic study reveals field-induced slow relaxation behavior of the magnetically isolated seven-coordinate Co^{II} centers with an easy-plane magnetic anisotropy.

2. Results and Discussion

The reaction of H₄daps ligand with methanolic solution of Co(ClO₄)₂·H₂O and aqueous solution of NaN(CN)₂ under ambient condition gave complex **1**. The final reaction was filtered after additional stirring for 3 h and then was kept for crystallization, which gave X-ray quality red crystals of complex **1** (for details procedure, see Materials and Methods section). Single-crystal X-ray analysis revealed that complex **1** crystallized in the orthorhombic *Pbca* space group (Table S1). The Co^{II} center is ligated around the equatorial plane by a pentadentate H₄daps ligand and the axial positions are occupied by the cyano N atoms of two crystallographically equivalent {N(CN)₂} units (Figure 1). The two N atoms of the bridging {N(CN)₂} moiety binds to Co^{II} center in a *cis*- μ_2 -*N*-coordination mode, resulting in an anti-configuration for the zigzag one-dimensional (1D) framework. Systematic analysis of the coordination geometry around the metal using SHAPE 2.1 [51] reveals that the seven-coordinate Co^{II} center displays a distorted pentagonal bipyramid coordination geometry (Figure S1) with a minimum CShM value of 0.244 (Table S2). The ligand bite angles range from 71.27(3)° (for N_{pyridyl}-Co-N) to 76.82(4)° (for O-Co-O) (Table S3). The shortest intra-chain Co...Co distance is 7.980(3) Å, whereas the shortest inter-chain Co...Co distance equals 10.674(2) Å. The chains run parallel to the crystallographic *c*-axis (Figure 1). Lattice methanol molecules are involved in intermolecular hydrogen bonding with the carbonyl oxygen atoms and phenoxy oxygen atoms of the ligand (Table S4). Additionally, there are significant π -interactions and hydrogen-bonding networks between the chains and the interstitial solvent molecules (methanol and acetonitrile), which also supports the formation of a supramolecular two dimensional arrangement (Figures S2–S4). The large intra and inter-chain Co...Co distances play a significant role to make them magnetically isolated seven-coordinate Co^{II} centers and allows us to measure the single ion magnetic behavior.

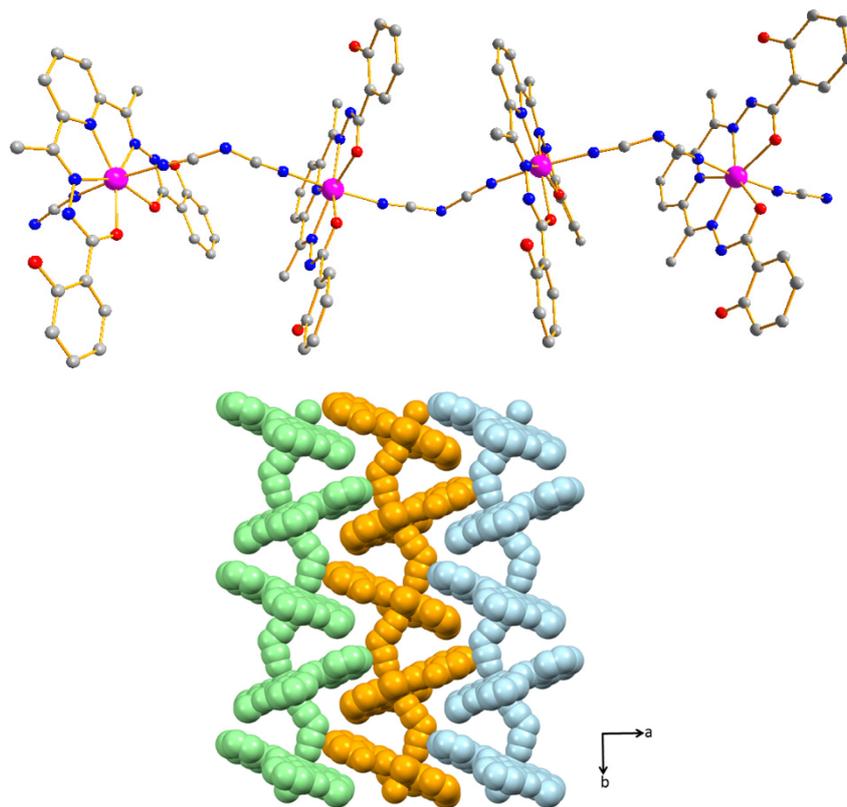


Figure 1. View of the molecular structure of complex **1** (top panel). Color codes: Co (magenta), O (red), N (blue), C (gray). Hydrogen atoms are omitted for clarity; Helical arrangement of **1** along the *c* axis (bottom panel).

Phase purity of complex **1** was confirmed by the good agreement of the bulk phase powder X-ray diffraction patterns which matches well with the simulated ones from crystal structure data (Figure S5). Magnetic susceptibility measurements were performed under direct current (DC) and an applied field of 0.1 T. At room temperature, the experimental $\chi_M T$ value (χ_M = molar magnetic susceptibility) of $2.76 \text{ cm}^3 \text{ K mol}^{-1}$ is larger than the spin-only value ($1.875 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, $S = 3/2$, $g = 2$) for a high-spin Co^{II} ion but falls well in the range of $2.1\text{--}3.4 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ as expected for a highly anisotropic Co^{II} ion with a significant orbital contribution [52]. Upon cooling from 300 K, the $\chi_M T$ value remains constant down to 150 K, below which it drastically decreases and reaches a value of $1.61 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K (Figure 2).

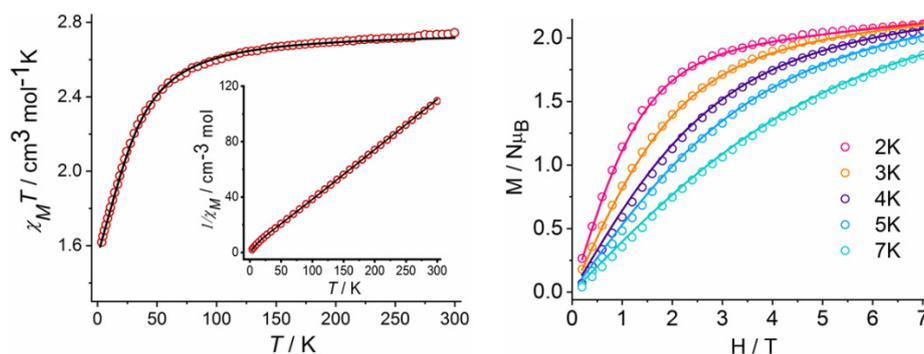


Figure 2. $\chi_M T$ vs. T plot measured at 0.1 T for complex **1** (left). The black line is the best fit; $M/N\mu_B$ vs. H plots for complex **1** (right) at the indicated temperatures. The solid lines are the best fit.

The decrease in the $\chi_M T$ curves at low temperatures may be due to the intrinsic magnetic anisotropy of the Co^{II} ions. Reduced magnetization data ($M/N\mu_B$ vs. H) were collected, and they

reached the highest value of $2.15 N\mu_B$ at 2 K and 7 T (Figure 2). This value is well below the theoretical saturation value of 3.3 for $S = 3/2$ system ($g = 2.2$). The magnetization values do not saturate even at the highest available fields and the $M/N\mu_B$ vs. H/T plots show that all isotherm magnetization plots do not collapse on the same master curve, indicating that the system has a strong magnetic anisotropy (Figure S6). The spin Hamiltonian of Equation (1) is used to define the magnetic anisotropy qualitatively.

$$\hat{H} = D \sum_{i=1}^2 \left[\hat{S}_z^2 - \frac{1}{3} S(S+1) \right] + E \sum_{i=1}^2 (\hat{S}_x^2 - \hat{S}_y^2) + \mu_B \cdot B \cdot g_{Co} \sum_{i=1}^2 S_i - J \hat{S}_1 \cdot \hat{S}_2 \quad (1)$$

where J is the exchange interaction between two adjacent Co^{II} centers; μ_B , S and B represent the Bohr magneton, spin ($S = 3/2$) and magnetic field vectors, respectively; D and E terms represent the single-ion axial and rhombic ZFS parameters. The PHI code [53] was used in order to calculate the anisotropy parameter by simultaneously fitting the susceptibility and the magnetization data. The best fit gave $D = 41.3(5) \text{ cm}^{-1}$, $E = 0.81(3) \text{ cm}^{-1}$ and $g_x = 2.29$, $g_y = 2.21$, $g_z = 1.98$ and very weak antiferromagnetic exchange interaction, $J = -0.004 \text{ cm}^{-1}$. The positive sign of the D parameter also agrees well with the other previously reported seven-coordinate Co^{II} complexes (Table S5) [41–50].

To further analyze the electronic structure and magnetic anisotropy of the complex, we performed quantum chemical calculation with ORCA 4.0 and MOLCAS 8.2 [54,55] (see Computational details). However, it has been observed that MOLCAS calculations show slightly higher anisotropic parameters (D and E) as compared to the ORCA calculations. This is because the dynamic correlation effect was employed (by NEVPT2) in ORCA, whereas we were unable to perform the CASPT2 calculations due to the limitation of our computational facility. The calculations show that the strong spin orbit coupling between the spin-free states reduces the energy of the spin-orbit states (Table S6). The ZFS parameters disclose that the lowest energy Kramers doublets (KDs) lead to easy-plane magnetic anisotropy as the g_x and g_y components of the g tensor are higher than the g_z components (Table 1). This is also in good agreement with the positive sign of D as estimated from the fitting of the experimental DC data shown in Table 1. For the Co^{II} system with axial anisotropy, the spin state with $S = 3/2$ splits in two Kramers doublets $\pm 1/2$ and $\pm 3/2$. The negative D stabilized $\pm 3/2$ doublets and the positive D stabilized $\pm 1/2$ doublets, which is also reflected in the anisotropy of the ground state ($g_x = 5.21$, $g_y = 4.37$, $g_z = 1.97$) Kramers doublets ($S = 1/2$) as obtained from ab initio calculation for the studied complex (Figure 3 and Table S7). Furthermore, the first excited state KDs is axial in nature ($\pm 3/2$), as the anisotropy is very close to the ideal value ($g_x = 0$, $g_y = 0$, $g_z = 6$, Table S6). In order to check the electronic transition and the splitting of the d orbital (Figure 3), we employed the ab initio ligand field theory (AILFT) approach by ORCA [16,26].

Table 1. ORCA/CASSCF, ORCA/CASSCF+NEVPT2 and MOLCAS/CASSCF+RAS-SO computed D , $|E|$ and main values of $g_{x,y,z}$ from the pseudospin Hamiltonian w.r.t. $\tilde{s} = 3/2$ for complex 1.

D_{fit} (cm^{-1})	E_{fit} (cm^{-1})	D_{calc} (cm^{-1}) ^a	D_{calc} (cm^{-1}) ^b	D_{calc} (cm^{-1}) ^c	E_{cal} (cm^{-1})	(g_{xyz}) ^b
41.3	0.81	39.11	35.72	43	1.68 ^a , 1.60 ^b , 2.28 ^c	2.32, 2.28, 1.99

^a = ORCA/CASSCF; ^b = ORCA/CASSCF/NEVPT2; ^c = CASSCF/RASSI-SO/Single_Aniso.

It is well known that if the ground and excited state have the same multiplicity and coupled through the $\hat{L}_+ \hat{S}_-$ or $\hat{L}_- \hat{S}_+$ part of the SOC operator, then they lead to positive or negative contribution to D . Usually, in the ideal PBP geometry, the electronic configuration for $\text{Co}(\text{II}) d^7$ system reveals that the electronic excitation occurs between the different m_l values of the d orbitals and results in easy-plane magnetic anisotropy (positive D) as reported in the literature (Figure 3a) [41–50]. In the studied complex, we found that the ground and excited states are multi configurational and none of them can be expressed by single determinant. It has been also observed that the quartet ground state

wave functions is more dominated (53%) by an electronic configuration of $(d_{xz})^1 (d_{yz})^2 (d_{xy})^1 (d_{x^2-y^2})^2 (d_z)^1$, which is also reflected in d-orbital splitting obtained from the AILFT (Figure 3b). However, the presence of the multiconfigurational nature of the wave function of the electronic states leads to the strong mixing among d orbitals for which the orbital splitting differs from the expected for ideal PBP geometry. On the other hand, the first excited state is dominated (31%) by an electronic configuration of $(d_{xz})^1 (d_{yz})^1 (d_{xy})^1 (d_{x^2-y^2})^2 (d_z)^2$. Thus, the ground and excited states differ only by the occupation of d_{yz} and d_z orbitals. In this case, the first excitation involved the transition between different m_l level from d_{yz} to d_{z^2} orbital (Figure 3b,c), which induces a coupling through the $\hat{L}_+ \hat{s}_- + \hat{L}_- \hat{s}_+$ part of the SOC operator, results in positive D value. Similarly, the contribution to D from the third and fourth excited states are also positive and much higher as compare to other states, whereas the large positive and negative contributions of E are from the third and fourth excited states, respectively (Table S8). It has been observed that both the same spin multiplicity and different multiplicity states contribute to the overall D value.

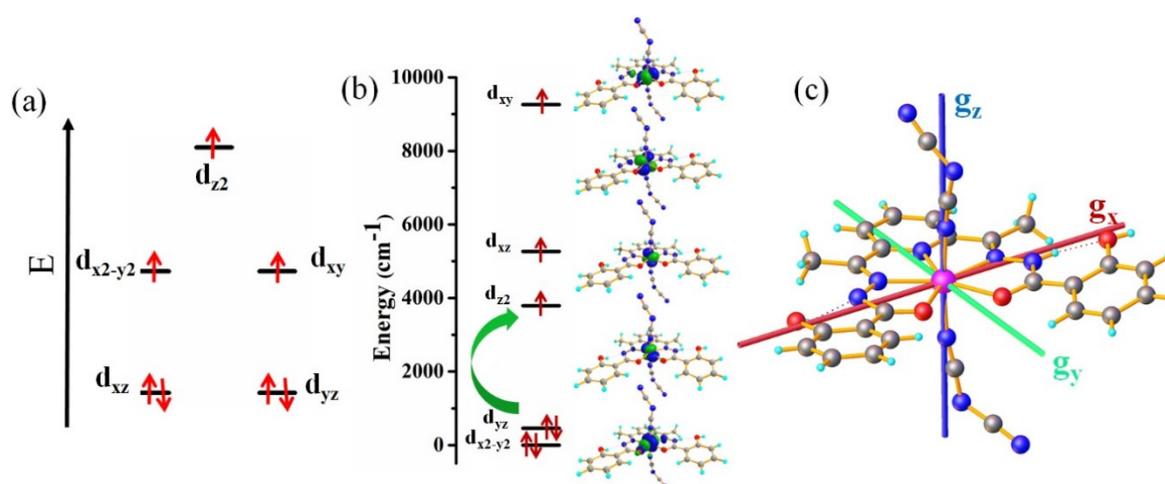


Figure 3. The splitting of the d-orbital on ideal PBP geometry (a); AILFT computed d-orbital splitting diagram (b) and orientation of the ground state anisotropy axis for complex **1** (c).

To investigate the dynamic magnetic behavior of complex **1**, the alternating current (ac) susceptibility measurements were performed with the temperature and frequency range of 2–10 K and 1–750 Hz respectively. No out-of-phase (χ_M'') signal on AC susceptibility was observed in the absence of an external magnetic field. This is probably due to strong QTM which leads to fast relaxation, as commonly observed in transition metal based SMMs [15]. Therefore, to reduce the QTM and check the optimum field, we measured the ac susceptibility at 2 K temperature to different external fields. The χ_M'' shows peak maxima around 0.22 T (Figure S7) and the AC susceptibility measurement was again performed for the same field.

However, no clear peak maxima were observed in the temperature as well as frequency dependence above 2 K within the frequency range of 1–800 Hz (Figure 4b).

This demonstrates the significant effect of QTM on the slow relaxation process, even under the most optimal DC field, and it is very common for Co^{II} -based SMMs, as reported earlier [46,47,56,57]. Although we have limitation in our instrument (frequency range 0–800 Hz) but the extrapolation of the frequency dependence plots up to 10,000 Hz using the Debye model shows clear peak maxima in both χ_M' and χ_M'' (Figure 4). This indicates the presence of field-induced slow relaxation of magnetization in complex **1**. The semicircle nature of the Cole-Cole plot [58–61] obtained from both χ_M' and χ_M'' reveals the single relaxation process and the generalized Debye model was used to extract the magnetization relaxation time (τ) with the associated width of the distribution (α) which displays narrow distribution of relaxation time ($\alpha = 0.21$ – 0.09). Furthermore, the fitting of the Arrhenius plot using $\ln(\tau) = \ln(\tau_0) + U_{\text{eff}}/KT$ equation gives $U_{\text{eff}} = 9.9$ K (6.88 cm^{-1}) and $\tau_0 = 5.3 \times 10^{-6}$ s (Figure S8). The obtained barrier

for spin reversal process is much lower than the energy of the first excited states (88 cm^{-1}). This clearly indicates that the relaxation process does not follow the Orbach process. Furthermore, to analyze the relaxation dynamics, we used the Single_Aniso module of MOLCAS (Figure 4d). It was found that the matrix element of the transition moment between the ground state KDs is somewhat larger ($1.5\ \mu_B$) than the required value ($0.1\ \mu_B$) for efficient relaxation.

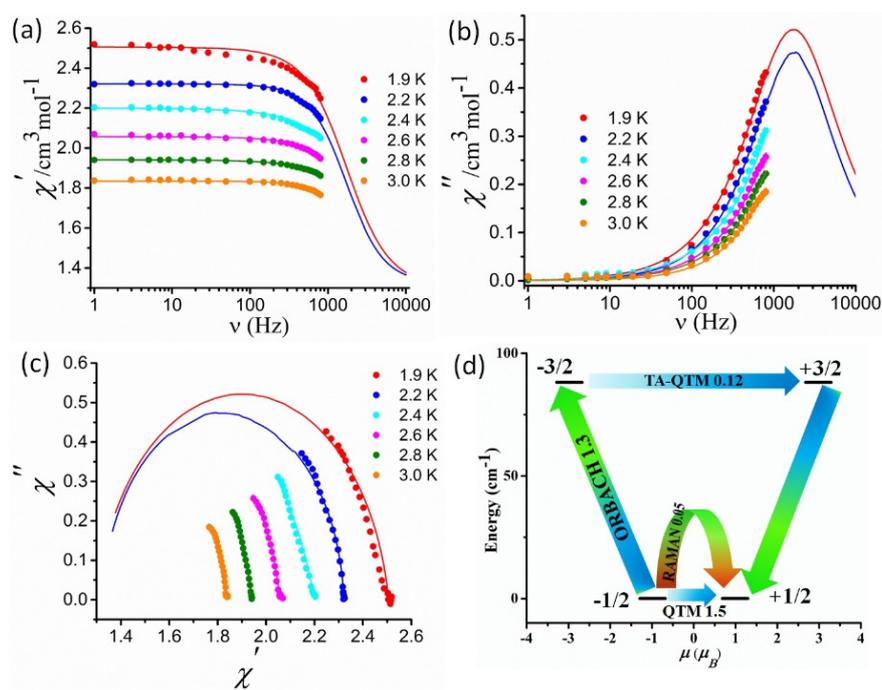


Figure 4. The frequency dependence of the in-phase (χ_M') (a) and out-of-phase (χ_M'') (b) AC magnetic susceptibility plots under 0.22 T external field; Cole-Cole plot complex 1 (c). Solid lines represent the best fit; lowest two Kramers' doublets and ab initio computed relaxation mechanism of complex 1 (d). The values shown in the arrows indicate the matrix elements of the transition magnetic moments (above 0.1 an efficient spin relaxation mechanism is expected).

Thus, it can be said that QTM plays a major role in the dynamic magnetic behavior of complex 1. On the other hand, the energy of the first excited state lies around 88 cm^{-1} , which is also quite large as compared to the observed energy barrier. This means that the relaxation process in 1 also follows some shortcut path through virtual states, called the Raman process, and results in barrier relaxation. So, in complex 1, the magnetization relaxation process is mainly controlled by QTM and the Raman process, as QTM cannot be suppressed completely as it is also dependent on some other factor such as hyperfine interaction, dipole–dipole interaction, etc. Furthermore, the second and third excited states have much higher energy (2189 and 2662 cm^{-1}) and demagnetization does not follow this path.

3. Materials and Methods

Magnetic measurements were performed using a Quantum Design SQUID-VSM magnetometer. The measured values were corrected for the experimentally measured contribution of the sample holder, while the derived susceptibilities were corrected for the diamagnetic contribution of the sample, estimated from Pascal's tables [62]. Elemental analysis was performed on Elementar Microvario Cube Elemental Analyzer. The infrared spectroscopy (IR) spectrum was recorded on KBr pellets with a Perkin-Elmer spectrometer. Powder X-ray diffraction (PXRD) data were collected on a PANalytical EMPYREAN instrument using Cu-K α radiation.

Synthesis of ligand: H_4daps was prepared by a simple hydrazine condensation reaction of one equivalent 2,6-diacetylpyridine with two equivalents of 2-salicyloylhydrazide in methanol according to a previously reported procedure [63].

Synthesis of complex 1: H₄daps (43 mg, 0.1 mmol) was dissolved in 5 mL of MeCN; then, triethylamine (10 mg, 0.1 mmol) was added dropwise to it. Then, 5 mL methanolic solution of Co(ClO₄)₂·H₂O (36 mg, 0.1 mmol) was added and the reaction mixture stirred. Then, 5 mL aqueous solution of NaN(CN)₂ (9 mg, 0.1 mmol) was added to the above reaction mixture. The whole mixture forms a red color and stirred for 3 h. Then, the solution was filtered and kept for slow evaporation for 3 days and gave X-ray quality red crystals of [Co(H₃daps)(dca)]·(MeOH)₂·(MeCN) (1). These were washed with ether, and the yield was calculated as 53%. Anal. Calcd for C₂₉H₃₁CoN₉O₆: C, 52.73; H, 4.73; N, 19.08%. Found: C, 52.80; H, 4.82; N, 19.15%. IR (KBr pellet, 4000–400 cm⁻¹) ν/cm⁻¹: 3422, 3073, 2917, 2818, 2175, 1529, 1384, 1318, 1289, 1076, 1028, 713.

Intensity data were collected on a Brüker APEX-II CCD diffractometer using a graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. Data collection was performed using φ and ω scans. The structure was solved using direct methods followed by full matrix least square refinements against F² (all data HKLF 4 format) using SHELXTL [64]. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi-scan absorption correction was applied. Non-hydrogen atoms were refined with independent anisotropic displacement parameters and hydrogen atoms were placed geometrically and refined using the riding model. All calculations were carried out using SHELXL 97 [65], PLATON 99 [66], and WinGX system Ver-1.64 [67]. Crystallographic data for complex 1 are summarized in Table S1.

All the calculations were performed using ORCA 4.0 [54] and MOLCAS 8.2 [55] software packages on the experimentally determined X-ray structure without optimization. In ORCA 4.0 we performed both the calculations CASSCF and CASSCF+NEVPT2 (Method of dynamic correlation effect), whereas only CASSCF/RASSI-SO/SINGLE_ANISO type calculations were performed. All the calculations were carried out with scalar relativistic effect with ZORA (zeroth-order regular approximation) in ORCA. We used the def2-TZVPP basis set for Co, def2-TZVP for N, O and def2-SV(P) for other atoms. An auxiliary def2/JK Coulomb fitting basis set was used during the calculation. The quasi-degenerate perturbation theory (QDPT) approach was used to introduce the spin-orbit coupling effects. We considered CAS (7,5) where 7 electrons in 5 'd' orbital and computed 10 quartets and 40 doublet. For the effect of dynamic correlation, we employed N-electron valence perturbation theory (NEVPT2) on top of the CASSCF wave functions. Both the zero-field splitting parameter (*D*) and transverse anisotropy (*E*) were calculated from second order perturbation theory and an effective Hamiltonian approach (EHA). For MOLCAS calculations, all atoms were described by the ANO-RCC basis sets of functions ([ANO-RCC-VTZP] for Co, [ANO-RCC-VTZ] for O, N and [ANO-RCC-VDZ] for C, H) including the relativistic effects within Douglas Kroll Hess Hamiltonian [68,69]. To save computational time and disk space, the Cholesky decomposition [70] of two-electron integrals has been used. In CASSCF [71] method 7 electrons in 5 'd' orbital was used to calculate all states (10 quartets and 40 doublets). The RASSI program was used to introduce spin orbit coupling by mixing of the optimized states in previous calculations. We were unable to performed CASPT2 calculations due to limitations in Computational facility. The SINGLE_ANISO [72] program was used to calculate the magnetic properties and the parameters of the pseudo-spin Hamiltonians describing the zero-field splitting.

4. Conclusions

In summary, SIM-type field-induced slow relaxation behavior of the magnetically isolated seven-coordinate Co^{II} centers in a 1D coordination polymer is reported. The easy-plane magnetic anisotropy was confirmed from both experimental and ab initio theoretical calculations. Besides reporting the single-ion-magnetic behavior with seven-coordinate Co^{II} centers, the present work also provides a new route to the design and synthesis of a stable magnetic material based on a mononuclear complex unit and toward the construction of multifunctional coordination polymer materials.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2312-7481/6/4/45/s1>. **Table S1:** X-ray Crystallographic Data and Refinement Parameters for complex **1**. **Figure S1:** Distorted pentagonal bipyramid coordination geometry around the Co^{II} center in **1**. **Table S2:** Summary of SHAPE analysis for complex **1**. **Table S3:** Bond distances (Å) and bond angles (°) around Co^{II} center found in complex **1**. **Figure S2:** A view of supramolecular 2D arrangement of complex **1** through intermolecular H-bonding and CH $\cdots\pi$ interactions. **Figure S3:** A view of de-solvated framework of **1** emphasizing the supramolecular interactions. **Figure S4:** Helical 1D arrangement of complex **1** along the *c* axis. **Table S4:** H-bond parameters found in complex **1**. **Figure S5:** PXRD for complex **1**. **Figure S6:** $M/N\mu_B$ vs. H/T plots at the indicated temperatures for complex **1**. The solid lines are the best fit. **Table S5:** Magnetic anisotropy (*D* parameters) and SIM parameters for previously reported seven-coordinated Co^{II} SIMs in the literature. **Table S6:** Ab initio calculated energies (cm⁻¹) of the lowest states ($S = 3/2$) of complex **1**. **Table S7:** Ab initio calculated magnetic anisotropy in the ground state and first excited state (w.r.t. $S = 1/2$) for complex **1**. **Table S8:** Energy of the first four excited states (cm⁻¹) and their contribution to the *D* and *E* values in cm⁻¹ at CAS(7,5) NEVPT2 level by ORCA. **Figure S7:** Frequency dependency of out-of-phase susceptibility at different external magnetic field (0–0.9 T) and 2 K temperature. **Figure S8:** $\ln(\tau)$ vs. $1/T$ plot for complex **1**.

Author Contributions: A.K.M. designed the project and performed all the experiments; A.K.M. solved the crystal structures and collected and analyzed the magnetic data; A.M. performed the theoretical calculations; A.K.M., A.M. and S.K. wrote the paper; S.K. supervised the overall project. All authors have read and agreed to the published version of the manuscript.

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