Magnetization Relaxation Dynamics of a Rare Coordinatively Unsaturated Co(II) Complex: Experimental and Theoretical Insights

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EXPERIMENTAL SECTION

Materials and General Methods.

Unless otherwise stated, all reactions were carried out under an inert (Argon) atmosphere. The Lithium (2,6-diisopropylphenyl)amide (L) ligand was prepared using the literature method.¹ THF, hexane, and DME solvents were dried with sodium and benzophenone and distilled prior to use.² All other chemicals were purchased from commercially available sources (Alfa Aesar and Sigma-Aldrich). Single-crystal data were collected on a Rigaku Saturn CCD diffractometer using a graphite monochromator (Mo K α , $\lambda = 0.71073$ Å). The selected crystals were mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced with an Oxford Cryo-cooling device. Complete hemispheres of data were collected using ω and φ scans (0.3°, 16 s per frame). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software, and they were corrected for absorption correction. Structure solution and refinement were performed with the SHELX package.³ The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F^2 . The magnetic susceptibility measurements were obtained with the use of an MPMS-XL SQUID magnetometer. Measurements were performed on polycrystalline samples and the magnetic data were corrected for the sample holder and diamagnetic contribution. Complex 1 is air and moisture sensitive, so the sample was prepared using a glove box under an argon atmosphere. The polycrystalline sample was grounded in an agate mortar pestle to make a fine powder. The fine powder was tightly wrapped in a piece of Teflon tape (~5 cm long). Finally, the Teflon wrapped sample was fixed inside the sample holder (straw) provided by the Quantum Design manufacturers of the MPMS-XL instrument. The ends of the straw were covered with Teflon tape and dipped into liquid nitrogen to avoid exposure to air/ moisture. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMX-plus (v = 9.35 GHz (X-band). The elemental analyses (CHN) were carried out on a Thermoquest microanalyser.

Synthesis of complex [Li(DME)₃][Co(L)₃] (complex 1):

Ligand (L) (0.2 g, 1.09 mmol) was dissolved into 10 ml of dry THF in a Schlenk tube. Anhydrous $CoBr_2$ (0.0795 g, 0.364 mmol) was added into the reaction mixture and it was stirred at room temperature for 24 hours. After stirring it for 24 hours THF was evaporated under vacuum and the target compound was extracted with dry hexane (6 mL) and it was filtered, then dry DME (~1 mL) was added drop by drop. It was kept at room temperature for the crystallization. The dark green color crystals were formed within 5 days and suitable for single X-ray studies. Yield: 0.025 g, 29.3% (Based on Co(II)). Elemental analysis (Argon dried sample) Calculated (%) C 66.64, H 9.79, N 4.86; Found (%) C 65.92, H 9.59, N 4.77.



[Li(DME)₃][Co(L)₃]

Scheme-S1: Synthetic procedure followed for complex 1.



Figure S1. Packing diagram of complex 1 (view along b-axis). Colour code: Green = Co(II), blue = N, grey = C, Pink = Li^+ and Red = O.

Formula	C ₄₈ H ₈₄ CoLiN ₃ O ₆
M/g.mol ⁻¹	865.05
Crystal system	Monoclinic
Space group	P21
a/ Å	10.8897(4)
b/ Å	21.2774(6)
c/ Å	11.9691(4)
α/ °	90°
β/ °	113.656(4)°
γ/ °	90°
V/ Å ³	2540.23(15)
Ζ	2
$\rho_{\text{calcd}}/\text{ mg.}\text{M}^3$	1.131
μ (Mo K α)/ mm ⁻¹	0.383
T/ K	100(2) K
Number of reflections	34157
Number of unique reflections	14276
R _{int}	0.0516
R_1, WR_2	0.0605, 0.1388
R_1, WR_2	0.0792, wR2 = 0.1711
GOF	1.145

 Table S1. Crystal data and structure refinement for complex 1.



Figure S2. Reduced magnetization plot of complex 1



Figure S3. Variable temperature EPR spectrum of complex 1 recorded in toluene at the indicated temperature.



Figure S4. Field sweep measurements performed on polycrystalline sample of complex 1 at 2 K



Figure S5. Frequency dependent in-phase and out-of-phase magnetic susceptibility of 1 in presence of dc field (H_{dc} = 500 Oe).

S.	Temperature	χs	χτ	τ	α	residual
No.	(K)					
1	2.0	0.124211E+00	0.699604E+00	0.116271E-01	0.287803E+00	0.432660E-03
2	2.2	0.114547E+00	0.646815E+00	0.897531E-02	0.284534E+00	0.484624E-03
3	2.4	0.104272E+00	0.591400E+00	0.660984E-02	0.279458E+00	0.827658E-03
4	2.6	0.974806E-01	0.547830E+00	0.508006E-02	0.273580E+00	0.135628E-02
5	2.8	0.932835E-01	0.509867E+00	0.392434E-02	0.260188E+00	0.198314E-02
6	3.0	0.896825E-01	0.476265E+00	0.303335E-02	0.249471E+00	0.237569E-02
7	4.0	0.872452E-01	0.359161E+00	0.908068E-03	0.175569E+00	0.221898E-02
8	5.0	0.829167E-01	0.287924E+00	0.281852E-03	0.956316E-01	0.310421E-03
9	6.0	0.858356E-01	0.242364E+00	0.776181E-04	0.458502E-01	0.689639E-04
10	7.0	0.412818E-01	0.209607E+00	0.141951E-04	0.864014E-01	0.167946E-03

 Table S2. Fitting parameters for Cole-Cole plot of complex 1.

$$\frac{1}{\tau} = AH^2T + CT^n + \tau_0^{-1} exp\left(\frac{-U_{eff}}{K_BT}\right)_{\dots \dots S1}$$

Computational details:

Multi-reference ab initio calculations were used to calculate the SH parameters. State-average Complete-Active-Space Self Consistent-Field (CASSCF) calculations were performed on the complex and dynamic correlations were included using NEVPT2 module, as implemented in the ORCA suite. The ZORA method was used for the treatment of scalar relativistic effects. The Ahlrichs polarized triple- ζ (TZVP) quality basis set, along with TZV/J auxiliary basis sets for the resolution of identity (RI) approximation, was used for all of the atoms. The calculations were performed with an active space of CAS (7,5), which corresponds to seven active d electrons in five active d orbitals and computed 10 quartets as well as 40 doublets in the Configuration Interaction (CI) procedure to extract the desired SH parameters.

Table S3. NEVPT2 computed SH parameters (g, D, and |E/D|) along with the State-by-State contributions to the D values for complex **1**.

	Energy (cm ⁻¹)	Contribution to D (cm ⁻¹)
	2619.5	28.34
	3020.1	24.39
	9369.8	-0.04
D _{total}	52.60	
E/D	0.07	
g ₁	1.98	
g ₂	2.58	
g ₃	2.67	

SH Parameters	2	3
D _{total}	+78.89	+72.29
E/D	0.01	0.01
g _x	1.89	1.93
gy	3.00	2.84
gz	3.02	2.89

Table S4. NEVPT2 computed SH Parameters (g, D, and |E/D|) along with the transition energies for complexes **2-3**.

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