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

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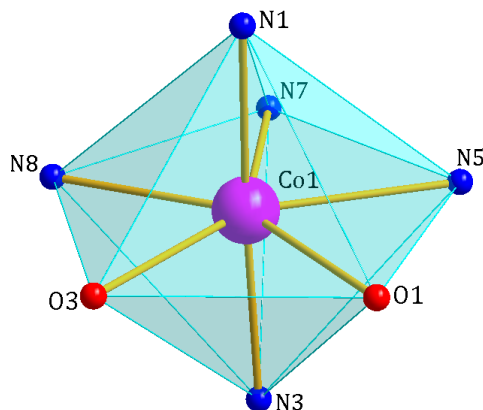
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Table S1. X-ray Crystallographic Data and Refinement Parameters for complex **1**.

	1
Formula	$C_{29}H_{31}CoN_9O_6$
M_w (g mol^{-1})	660.56
Crystal size (mm)	0.45×0.18×0.16
Crystal system	Orthorhombic
Space group	*Pbca*
T (K)	293(2)
a (Å)	19.6105(6)
b (Å)	15.8275(5)
c (Å)	20.3903(6)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	6328.9(3)
Z	8
ρ_{calcd} (g cm^{-3})	1.387
μ(MoKα) (mm^{-1})	0.598
F(000)	2744.0
T_{max}, T_{min}	0.919, 0.869
h, k, l range	$-26 \leq h \leq 26$, $-21 \leq k \leq 21$, $-27 \leq l \leq 27$
Collected reflections	7676
Independent reflections	5767
Goodness-of-fit (GOF) on F^2	1.095
R1, wR2 (I > 2σI)	0.0607, 0.1813

R1, wR2 (all data)	0.0812, 0.1970	
CCDC Number	1487267	

R1 = Σ||Fo| - |Fc||/Σ|Fo| and wR2= |Σw(|Fo|^2 - |Fc|^2)|/Σ|w(Fo)^2|$^{1/2}$

Figure S1. Distorted pentagonal bipyramid coordination geometry around the Co^{II} center in **1**.

Table S2. Summary of SHAPE analysis for complex **1**.

HP-7	1	D$_{7h}$	Heptagon
HPY-7	2	C$_{6v}$	Hexagonal pyramid
PBPY-7	3	D$_{5h}$	Pentagonal bipyramid
COC-7	4	C$_{3v}$	Capped octahedron
CTPR-7	5	C$_{2v}$	Capped trigonal prism
JPBPY-7	6	D$_{5h}$	Johnson pentagonal bipyramid J13
JETPY-7	7	C$_{3v}$	Johnson elongated triangular pyramid J7

Structure [ML$_7$]	HP-7	HPY-7	PBPY-7	COC-7	CTPR-7	JPBPY-7	JETPY-7
Complex **1**	33.909	23.175	**0.244**	7.271	5.752	2.952	23.537

Table S3. Bond distances (Å) and bond angles (°) around Co^{II} center found in complex **1**.

Bond distance (Å)			Bond angle (°)		
Complex **1**	Co1—O1	2.2315(1)	Complex **1**	O1—Co1—O3	76.82(5)
	Co1—O3	2.1897(1)		O1—Co1—N1	87.80(5)
	Co1—N1	2.0829(1)		O1—Co1—N5	70.62(5)
	Co1—N5	2.2149(1)		O1—Co1—N7	139.44(5)
	Co1—N7	2.2035(1)		O1—Co1—N8	149.21(5)
	Co1—N8	2.1408(1)		O1—Co1—N3	85.51(5)
	Co1—N3	2.0813(1)		O3—Co1—N1	89.61(5)
				O3—Co1—N5	147.38(5)
				O3—Co1—N7	143.73(6)
				O3—Co1—N8	72.40(6)
				O3—Co1—N3	87.57(6)
				N1—Co1—N5	91.11(6)
				N1—Co1—N7	92.04(6)
				N1—Co1—N8	92.80(6)

N1—Co1—N3	173.18(6)
N5—Co1—N7	68.84(6)
N5—Co1—N8	140.08(6)
N5—Co1—N3	87.93(6)
N7—Co1—N8	71.33(5)
N7—Co1—N3	93.91(5)
N8—Co1—N3	92.27(5)
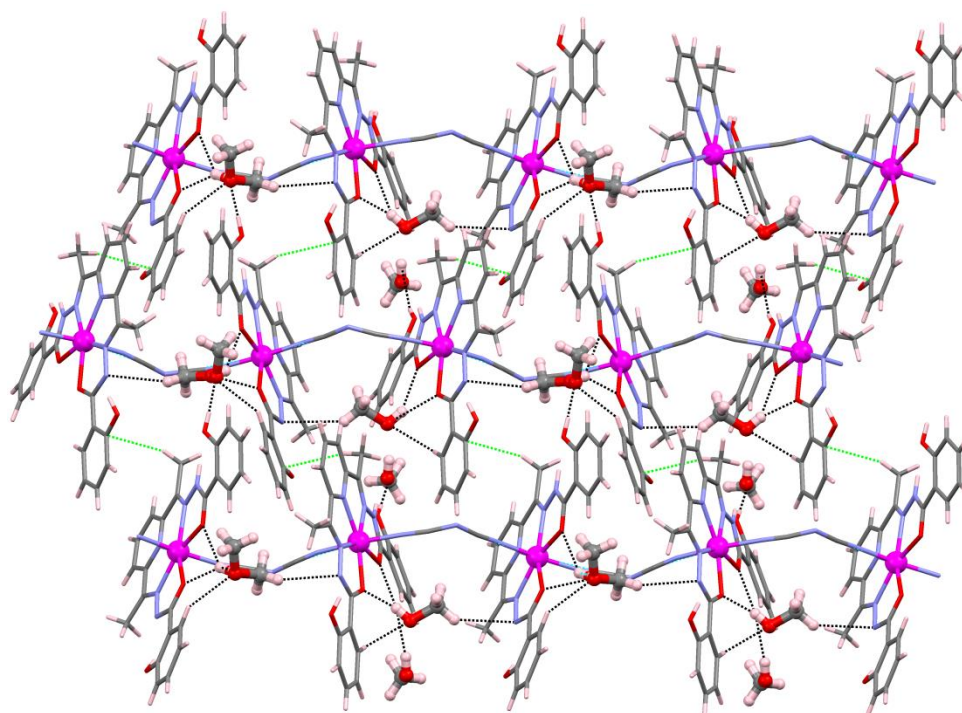
Figure S2. A view of supramolecular 2D arrangement of complex **1** through intermolecular H-bonding and CH···π interactions.
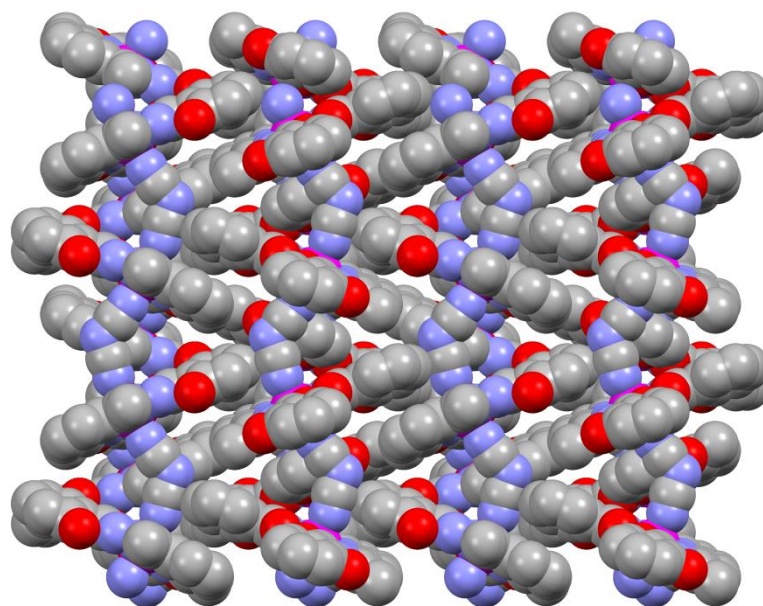
Figure S3. A view of de-solvated framework of **1** emphasizing the supramolecular interactions.
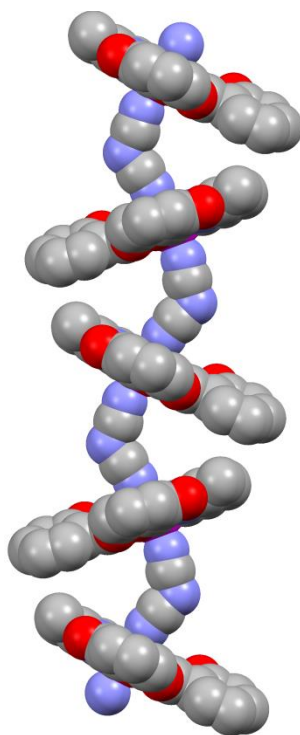
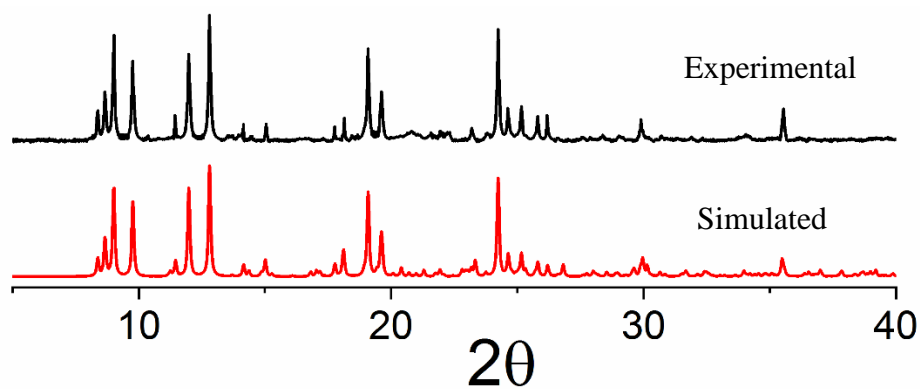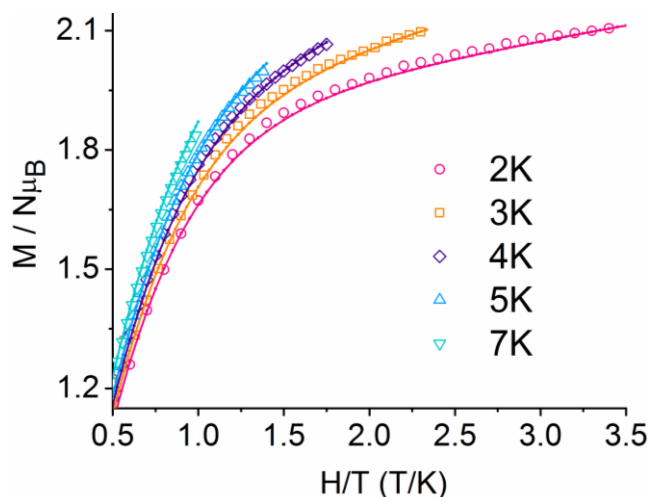**Figure S4**. Helical 1D arrangement of complex **1** along the *c* axis.

Table S4. H-bond parameters found in complex **1.**

D– H···A	D–H(Å)	H···A(Å)	D···A (Å)	<D-H-A(°)	Symmetry[#]
O5—H5···O1	0.82	2.39	3.070(4)	141	0
O5—H5···O3	0.82	2.14	2.834(4)	143	0
C54—H54A···O3	0.96	2.51	3.395(6)	154	0
O2—H2···O32A	0.82	1.76	2.550(4)	162	1
C2—H2A···N4	0.93	2.48	3.397(7)	168	2
O32A—H32A···O5	0.82	1.87	2.668(4)	165	3

(0) x,y,z; (1) 1/2+x,y,1/2-z; (2) 1/2-x,1-y,-1/2+z; (3) -1/2+x,1/2-y,1-z.

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.

Complex	D (cm^{-1})	τ_0 (s)	U_{eff} (K)	Ref.
[Co(dapbhH$_2$)(H$_2$O)(NO$_3$)](NO$_3$)	32.4	6.0×10^{-10}	81.2	1, 2
[CoL$_{N5}$(H$_2$O)$_2$]Cl$_2$·4H$_2$O	24.6	1.2×10^{-6}	29.8	2
[Co(dapbhH$_2$)(im)$_2$]·H$_2$O	24.8	8.7×10^{-11}	89.6	2
[Co(dapbhH$_2$)I(NO$_3$)]I	30	nr	nr	3
[Co(dapbhH$_2$)Br(NO$_3$)]Br	30	nr	nr	3
[Co(L$_1$)Cl$_2$]	40	nr	nr	4
[Co(L$_2$)](ClO$_4$)$_2$	26	nr	nr	5
[Co(L$_2$)](NO$_3$)$_2$	25	nr	nr	5
[Co(dapbhH$_2$)(SCN)$_2$]	15.9	nr	nr	6
[Co(dapbh)(H$_2$O)$_2$]	13.1	nr	nr	6
[Co(L)Cl$_2$]·2CH$_3$OH	38	1.1×10^{-5}	7.9	7
[Co(L)Br$_2$]	41	1.1×10^{-5}	6.1	7
[Co(L)I$_2$]	35	1.1×10^{-5}	6.5	7
[Co(tdmmb)(H$_2$O)$_2$][BF$_4$]$_2$	25.6	1.1×10^{-6}	42.2	8
[Co(tdmmb)(CN)$_2$]·2H$_2$O	17.4	3.2×10^{-7}	48.9	8
[Co(tdmmb)(NCS)$_2$]	26.3	1.0×10^{-6}	49.2	8
[Co(tdmmb)(SPh)$_2$]	34.5	2.1×10^{-7}	54.7	8
[Co(4-tert-butylpyridine)$_3$(NO$_3$)$_2$]	35.8	3.7×10^{-9}	52.6	9
[Co(isoquinoline)$_3$(NO$_3$)$_2$]	35.7	9.1×10^{-8}	28.8	9
[(OTftpy)Co(κ_2-O$_2$NO)$_2$]	-41.4	nr	nr	10
[Co(H$_2$daps)(MeOH)$_2$]	43.1	7.4×10^{-6}	33.5	11
[Co(H$_4$daps)(NCS)(MeOH)]·(ClO$_4$)·(MeOH)	41.5	5.6×10^{-6}	28.4	11
[Co(H$_4$daps)(NCS)$_2$]·(MeOH)$_2$	38.8	4.8×10^{-6}	23.6	11
[Co-(DAPBH)(NO$_3$)(H$_2$O)](NO$_3$)	30	nr	50	12
[Co(H$_4$L)(DMF)(H$_2$O)](NO$_3$)$_2$·(DMF)	35.9	6.5×10^{-6}	25	13
[Co(H$_4$L)(MeOH)(H$_2$O)](NO$_3$)$_2$·(MeOH)	37.2	3.5×10^{-6}	15	13
[Co(H$_4$L)(DEF)(H$_2$O)] (NO$_3$)$_2$	43.7	1.9×10^{-6}	4	13
[Co(H$_3$daps)(dca)]·(MeOH)$_2$·(MeCN)	41.3	5.3×10^{-6}	9.9	This paper

nr = not reported.

**Table S6.** Ab initio calculated energies (cm^{-1}) of the lowest states (S = 3/2) of complex **1**.

spin-free states	Spin-orbit states
0.000	0.000
2667.229	0.000
2917.222	88.169
4420.566	88.169
5045.421	2189.501
11036.401	2189.501
12350.207	2662.497
16705.986	2662.497
17772.836	3175.830
19500.981	3175.830
	3529.968
	3529.968

Table S7. Ab initio calculated magnetic anisotropy in the ground state and first excited state (w.r.t. $\tilde{s} = 1/2$) for complex **1**.

| Ground state	First excited state
g$_x$= 5.21	g$_x$= 0.37
g$_y$= 4.37	g$_y$= 0.37
g$_z$= 1.97	g$_z$= 5.96

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.

State	Mult	Complex **1**		
		Energy	D	E
1st	4	3663.5	2.955	-0.454
2nd	4	4049.8	0.868	0.385
3rd	4	5839.4	13.713	11.159
4th	4	6652.6	11.105	-9.458
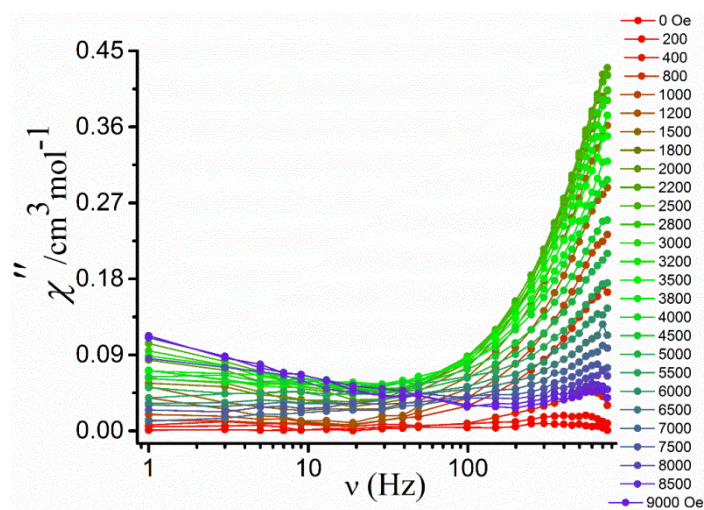
Figure S7. Frequency dependency of out-of-phase susceptibility at different external magnetic field (0-0.9 T) and 2 K temperature.
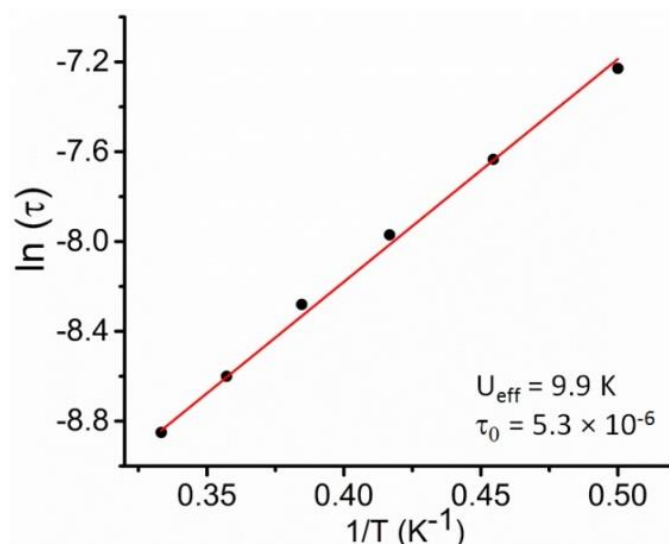
Figure S8. $\ln(\tau)$ *vs* 1/T plot for complex **1**.

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