Field-induced single ion magnet behaviour of hexacoordinated Co(II) complex with easy-axis type magnetic anisotropy

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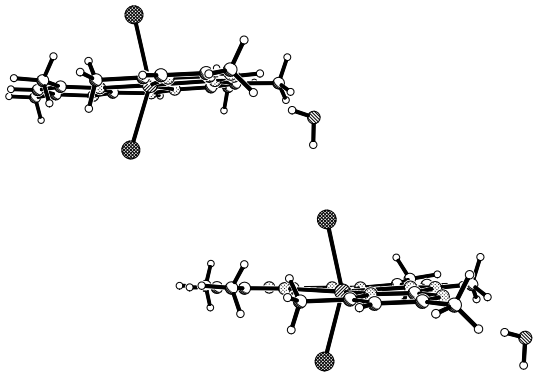
Electronic Supplementary Information



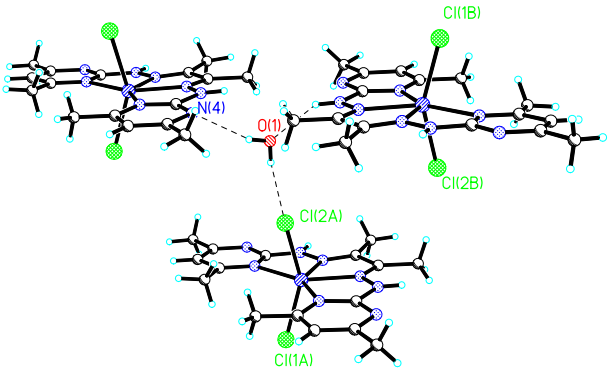
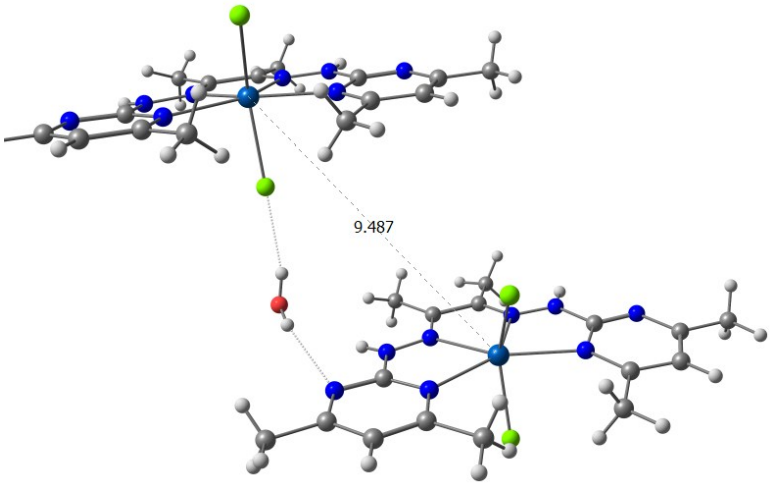


Figure S1. Intermolecular hydrogen bonds in crystalline state of I.



$J = +0.002$ cm^{-1}

Fig. S2: Hydrogen bonded dimer, extracted from crystalline structure of I. Calculated J value for Spin Hamiltonian $\hat{H} = -J \cdot \hat{S}_1 \cdot \hat{S}_2$ within broken symmetry approach (B3LYP/6-311G(d) level of theory).

It can be mentioned that nitrogen atom N(7) of the pyrimidine moiety does not participate in any intermolecular contacts in contrast to the chemically equivalent N(4) atom, within the range 3.10 Å around it there are no atoms of neighboring molecules. Consequently, minor, but noticeable shortening of the bond lengths formed by that atom (N(7)-C(11) and N(7)-C(12), 1.329(3) and 1.345(3) Å, respectively) is observed, in comparison with bonds formed by N(4) atom (N(4)-C(3) and N(4)-C(6), 1.341(3) and 1.350(3) Å, correspondingly), for which hydrogen bond is formed.

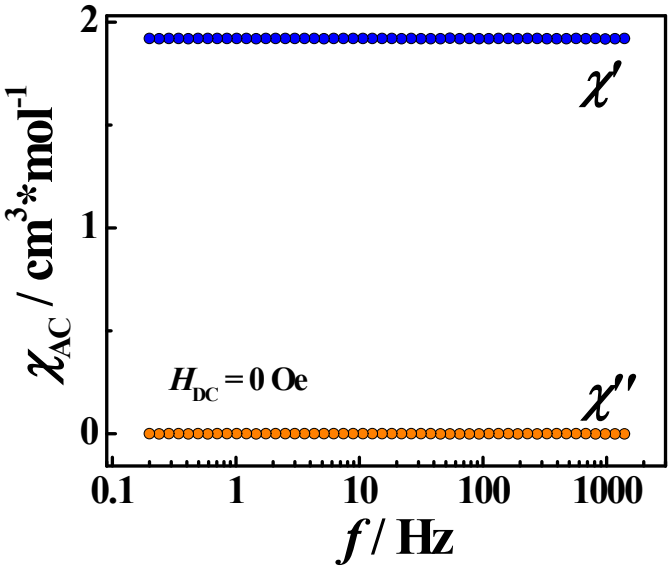


Fig. S3: Frequency dependence of the in-phase χ' and out-of-phase χ'' AC susceptibility χ_M at T=2K and H_{DC}=0 Oe for **I**.

Table S1. Crystallographic data for $[CoLCl_2]\cdot H_2O$

Empirical formula, moieties	C16 H22 Cl2 Co N8, H2O
Empirical formula, sum	C16 H24 Cl2 Co N8 O
Formula weight	474.26
Crystal size (mm)	0.35 × 0.31 × 0.27
Temperature (K)	150.0(1) K
Crystal system	Triclinic
Space group	P1
a (Å)	7.3262(3)
b (Å)	9.4868(5)
c (Å)	15.4805(6)
α (°)	103.132(4)
β (°)	90.420(3)
γ (°)	103.849(4)
V (Å^3)	1015.17(8)
Z	2
d_{calc} (Mg/m^3)	1.552
Absorption coefficient (mm^{-1})	1.134
F(000)	490
$2\theta_{min}$, deg	5.74
$2\theta_{max}$, deg	56.98

Reflections collected	10088
Independent reflections	5352
Reflections with $F^2>4\sigma(F^2)$	4338
Index ranges	$-9 < h < 9$ $-12 < k < 12$ $-21 < l < 17$
Number of refined parameters	253
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0405$, $wR_2 = 0.0784$
R indices (all data)	$R_1 = 0.0572$, $wR_2 = 0.0841$
Goodness-of-fit on F^2	1.032
Largest difference in peak and hole (eÅ^{-3})	0.45 / -0.46

Table S2. Selected bond lengths [Å] and angles [deg] for compound **I**.

Bond	Value, Å	Angle	Value, deg
Co(1)-N(5)	2.1561(17)	N(5)-Co(1)-N(1)	71.23(7)
Co(1)-N(1)	2.1848(18)	N(5)-Co(1)-Cl(1)	106.35(5)
Co(1)-Cl(1)	2.3196(6)	N(1)-Co(1)-Cl(1)	108.59(5)
Co(1)-N(3)	2.3221(18)	N(5)-Co(1)-N(3)	141.95(7)
Co(1)-N(8)	2.3245(18)	N(1)-Co(1)-N(3)	70.73(6)
Co(1)-Cl(2)	2.4010(6)	Cl(1)-Co(1)-N(3)	84.99(4)
N(1)-C(1)	1.297(3)	N(5)-Co(1)-N(8)	71.55(6)
N(1)-N(2)	1.355(2)	N(1)-Co(1)-N(8)	142.54(6)
N(2)-C(3)	1.376(3)	Cl(1)-Co(1)-N(8)	85.88(4)
N(3)-C(3)	1.337(3)	N(3)-Co(1)-N(8)	146.42(6)
N(3)-C(4)	1.354(3)	N(5)-Co(1)-Cl(2)	100.06(5)
N(4)-C(3)	1.341(3)	N(1)-Co(1)-Cl(2)	98.45(5)
N(4)-C(6)	1.350(3)	Cl(1)-Co(1)-Cl(2)	146.93(2)
N(5)-C(9)	1.287(3)	N(3)-Co(1)-Cl(2)	86.36(4)
N(5)-N(6)	1.355(2)	N(8)-Co(1)-Cl(2)	83.91(4)
N(6)-C(11)	1.375(3)	C(1)-N(1)-N(2)	120.66(18)
N(7)-C(11)	1.329(3)	C(1)-N(1)-Co(1)	119.79(15)
N(7)-C(12)	1.345(3)	N(2)-N(1)-Co(1)	119.52(13)
N(8)-C(11)	1.339(3)	N(1)-N(2)-C(3)	117.08(18)
N(8)-C(14)	1.351(3)	C(3)-N(3)-C(4)	115.06(19)
O(1)-H(11)	0.8895	C(3)-N(3)-Co(1)	115.08(13)
O(1)-H(12)	0.8507	C(4)-N(3)-Co(1)	129.73(15)
C(1)-C(9)	1.476(3)	C(3)-N(4)-C(6)	115.27(19)
C(1)-C(2)	1.497(3)	C(9)-N(5)-N(6)	119.97(18)
C(4)-C(5)	1.379(3)	C(9)-N(5)-Co(1)	120.89(15)
C(4)-C(7)	1.493(3)	N(6)-N(5)-Co(1)	119.10(13)
C(5)-C(6)	1.382(3)	N(5)-N(6)-C(11)	117.89(17)

C(6)-C(8)	1.500(3)	C(11)-N(7)-C(12)	115.63(19)
C(9)-C(10)	1.496(3)	C(11)-N(8)-C(14)	115.18(19)
C(12)-C(13)	1.390(3)	C(11)-N(8)-Co(1)	114.03(14)
C(12)-C(16)	1.495(3)	C(14)-N(8)-Co(1)	130.76(14)
C(13)-C(14)	1.391(3)	N(1)-C(1)-C(9)	113.67(18)
C(14)-C(15)	1.491(3)	N(1)-C(1)-C(2)	125.2(2)
		C(9)-C(1)-C(2)	121.10(18)
		N(3)-C(3)-N(4)	128.45(19)
		N(3)-C(3)-N(2)	117.47(19)
		N(4)-C(3)-N(2)	114.08(19)
		N(3)-C(4)-C(5)	121.1(2)
		N(3)-C(4)-C(7)	117.5(2)
		C(5)-C(4)-C(7)	121.48(19)
		C(4)-C(5)-C(6)	119.3(2)
		N(4)-C(6)-C(5)	120.9(2)
		N(4)-C(6)-C(8)	117.1(2)
		C(5)-C(6)-C(8)	122.05(19)
		N(5)-C(9)-C(1)	114.32(18)
		N(5)-C(9)-C(10)	124.1(2)
		C(1)-C(9)-C(10)	121.59(18)
		N(7)-C(11)-N(8)	128.65(19)
		N(7)-C(11)-N(6)	114.05(18)
		N(8)-C(11)-N(6)	117.29(19)
		N(7)-C(12)-C(13)	121.0(2)
		N(7)-C(12)-C(16)	116.3(2)
		C(13)-C(12)-C(16)	122.7(2)
		C(12)-C(13)-C(14)	118.6(2)
		N(8)-C(14)-C(13)	120.92(19)
		N(8)-C(14)-C(15)	116.94(19)
		C(13)-C(14)-C(15)	122.14(19)

Table S3. Best fit parameters of the two-component Debye model for the Cole-Cole plot of complex **I** at H_{DC} =3200 Oe

T, K	χ_S, $cm^3\ mol^{-1}$	$\Delta\chi_{T1}$, $cm^3\ mol^{-1}$	τ_1, s	α_1	$\Delta\chi_{T2}$, $cm^3\ mol^{-1}$	τ_2, s	α_2	R_1 [a]	x_1 [b]
2	0.68	0.49	0.316	0.346	0.72	1.15E-03	0.105	8.5E-03	0.68
2.5	0.52	0.40	0.229	0.270	0.72	8.77E-04	0.139	1.1E-03	0.56
3	0.46	0.25	0.180	0.257	0.70	7.00E-04	0.141	1.2E-03	0.36
4	0.37	0.10	0.155	0.231	0.68	4.55E-04	0.101	3.5E-04	0.15
5					0.63	2.55E-04	0.064	2.0E-04	
7					0.64	3.53E-05	0.063	1.2E-04	

[a] The mean residual sum of squares, $R_1 = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_{exp} - Y_{calc})^2}{Y_{exp}^{\ 2}}$.

[b] $x_1 = (\chi_{T1}-\chi_S)/(\chi_{T2}-\chi_S) = \Delta\chi_{T1}/\Delta\chi_{T2}$ - mole fraction of the low-frequency phase

Table S4. Best fit parameters of the one-component Debye model for the Cole-Cole plot of complex **I** at H_{DC} =1000 Oe

T, K	χ_S, $cm^3\ mol^{-1}$	χ_T, $cm^3\ mol^{-1}$	τ, s	α	R_1 [a]
2	1.67	1.88	2.72E-03	0.09	6.6E-04
2.5	1.38	1.63	1.97E-03	0.11	5.1E-04
3	1.13	1.40	1.42E-03	0.11	1.9E-03
4	0.92	1.18	7.87E-04	0.07	2.4E-03
5	0.74	0.95	2.88E-04	0.06	8.1E-05
7	0.15	0.72	0.41E-05	0.20	2.3E-04

[a] The mean residual sum of squares, $R_1 = \frac{1}{n}\sum_{i=1}^{n}\frac{(Y_{exp} - Y_{calc})^2}{Y_{exp}^{\ 2}}$

Table S5. Atomic coordinates used for ZFS calculations (hydrogen atoms positions optimized at BP86/def2-TZVP level of theory while non-hydrogen atoms are fixed at positions obtained from single crystal X-ray diffraction study)

Co	1.18971914813404	2.43824272001278	3.84869710627750
Cl	-0.18186259214886	4.12032682083468	4.87545033051699
Cl	1.70312603817490	1.26161553675098	1.91678473236533
N	1.37317279635709	1.08766976188048	5.55623357669205
N	0.38913896411349	0.19057695262195	5.80699390632533
H	0.43478349364151	-0.51209342526760	6.54313480126880
N	-0.68055087277282	1.06532175307572	3.94447962065723
N	-1.56420952826155	-0.80589356092489	5.18239033099433
N	3.06463116477177	2.82456176766218	4.84034618643296
N	3.87067086616076	3.80531768789111	4.36719120526593
H	4.77262137208214	4.04039543629593	4.77742010583841
N	4.26256515019149	5.50011373367696	2.91056151909313
N	2.20865441834349	4.25301259632579	2.81373561504133
C	2.43947701097685	1.12329712545256	6.29433060448735
C	2.72670228634025	0.20499507096314	7.44068740399518
H	2.41970090343034	-0.82863481945039	7.20790531570810
H	2.18891067241559	0.50406453885503	8.35702597872827
H	3.79344698813122	0.16410767769881	7.67743115233871
C	-0.66778378417222	0.15769447247272	4.92581307535958
C	-1.74498699609382	0.99348631268115	3.11115001411065
C	-2.72398558207923	0.03839574909009	3.28848089523873

H	-3.57450919880330	-0.00342684911136	2.60728037582524
C	-2.61970349195841	-0.84950357400545	4.34197351914159
C	-1.80435316554295	1.97173132518225	1.98475525656382
H	-1.77890301839432	2.99609505272922	2.38491459635777
H	-2.71269016097494	1.83496979081578	1.38526128894037
H	-0.91360614862493	1.84540534805283	1.35048521668649
C	-3.66027215437701	-1.89663921947313	4.60698515221548
H	-3.19463878349035	-2.89016165574136	4.67680652305440
H	-4.42656626539648	-1.91335407757991	3.82153651219807
H	-4.15288993113895	-1.70736197486248	5.57323684614464
C	3.40220793594393	2.16831765791826	5.89469905576965
C	4.63664002973317	2.44344348328765	6.69427589449769
H	5.55218758871295	2.11862626366369	6.16870636313834
H	4.62043766291059	1.94641987065127	7.66705338182412
H	4.74096926099399	3.52362835572344	6.89339771609101
C	3.42101289719801	4.54887626252242	3.30120918712917
C	3.83934040012566	6.26958446917665	1.89236168009109
C	2.60132002031852	6.05327420353336	1.29829450340347
H	2.25492989980073	6.67741564366265	0.47521096957315
C	1.79671444547130	5.02929565848039	1.78783944106740
C	0.44372933711223	4.74673187569154	1.22892002039638
H	-0.29584050311531	4.79748824927277	2.04347755958245
H	0.41954255430901	3.72253898940412	0.82772878820242
H	0.17643789212494	5.45763845335371	0.43801324288670
C	4.77112355671134	7.35134349797880	1.44797253143042
H	5.73406457093274	6.91959402910271	1.13778872234600
H	4.98500502193132	8.03614829278198	2.28223927987638
H	4.35730982975006	7.92963666918903	0.61256789883039