Supplementary Material

Field Induced Single Ion Magnetic Behaviour in Square-pyramidal Cobalt(II) Complexes with Easy-plane Magnetic Anisotropy

Table S1. X-ray Crystallographic Data and Refinement Parameters for complexes **1** and **2**.

	1	**2**
Formula	$C_{14}H_{32}ClCoN_4F_4B$	$C_{38}H_{47}Cl_2CoN_5O_4$
M_w (g mol^{-1})	437.63	767.64
Crystal size (mm)	0.50×0.19×0.15	0.44×0.16×0.15
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$C2/c$
T (K)	148(2)	139(2)
a (Å)	8.2356(12)	34.573(3)
b (Å)	14.849(2)	14.1926(11)
c (Å)	8.4147(14)	16.0044(11)
(°)	90.00	90.00
(°)	109.245(8)	113.669(4)
(°)	90.00	90.00
V (Å^3)	971.5(3)	7192.5(10)
Z	2	8
ρ_{calcd} (g cm^{-3})	1.496	1.417
μ(MoKα) (mm^{-1})	1.062	0.674
F(000)	458.0	3224.0
T_{max}, T_{min}	0.863, 0.775	0.914, 0.889
h, k, l range	$-10 \le h \le 10$, $-18 \le k \le 18$, $-10 \le l \le 10$	$-46 \le h \le 46$, $-19 \le k \le 19$, $-21 \le l \le 21$
Collected reflections	2908	6696
Independent reflections	2316	6082
Goodness-of-fit (GOF) on F^2	1.064	1.011
R1, wR2 (I > 2σI)	0.0636, 0.1576	0.0617, 0.1613
R1, wR2 (all data)	0.0849, 0.1673	0.0672, 0.1667
CCDC Number	1458031	1455062

$R1 = \Sigma||Fo|-|Fc||/\Sigma|Fo|$ and $wR2= |\Sigma w(|Fo|^2-|Fc|^2)|/\Sigma|w(Fo)^2|^{1/2}$.

Table S2. Bond distances (Å) and bond angles (°) around Co^{II} centers found in complex **1** and **2**.

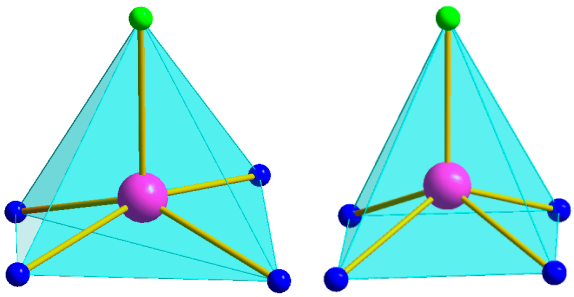
		Bond distance (Å)			
Complex 1	**Co – N1**	**2.1518(1)**	**Complex 2**	**Co – N2**	2.1485(1)
	Co – N2	2.1972(1)		Co – N3	2.1808(1)
	Co – N3	2.1433(1)		Co – N4	2.1541(1)
	Co – N4	2.1618(1)		Co – N5	2.1754(1)
	Co – Cl1	2.2850(1)		Co – Cl2	2.2447(1)
		Bond angle (°)			
Complex **1**	Cl1—Co1—N2	98.91(6)	Complex **2**	Cl2—Co1—N2	115.38(4)
	Cl1—Co1—N1	105.48(5)		Cl2—Co1—N3	105.45(4)
	Cl1—Co1—N4	98.33(5)		Cl2—Co1—N5	118.47(4)
	Cl1—Co1—N3	108.07(5)		Cl2—Co1—N4	108.62(6)
	N2—Co1—N1	91.26(6)		N2—Co1—N3	81.59(6)
	N2—Co1—N4	162.74(6)		N2—Co1—N5	82.28(5)
	N2—Co1—N3	82.71(5)		N2—Co1—N4	135.62(4)
	N1—Co1—N4	83.36(5)		N3—Co1—N5	135.99(5)
	N1—Co1—N3	146.43(5)		N3—Co1—N4	81.63(4)
	N4—Co1—N3	92.72(6)		N5—Co1—N4	81.96(4)

Shape analysis

Table S3. Summary of SHAPE analysis for complexes **1**-**2**.

PP-5	1	D_{5h}	Pentagon
vOC-5	2	C_{4v}	Vacant octahedron
TBPY-5	3	D_{3h}	Trigonal bipyramid
SPY-5	4	C_{4v}	Spherical square pyramid
JTBPY-5	5	D_{3h}	Johnson trigonal bipyramid J12

Structure [ML_5]	**PP-5**	**vOC-5**	**TBPY-5**	**SPY-5**	**JTBPY-5**
Complex **1**	32.439	2.186	3.037	**0.558**	5.891
Complex **2**	32.028	4.674	5.931	**0.846**	9.781



(left) (right)

Figure S1. Distorted square-pyramidal coordination geometry around the Co^{II} centers in **1** (left) and **2** (right).

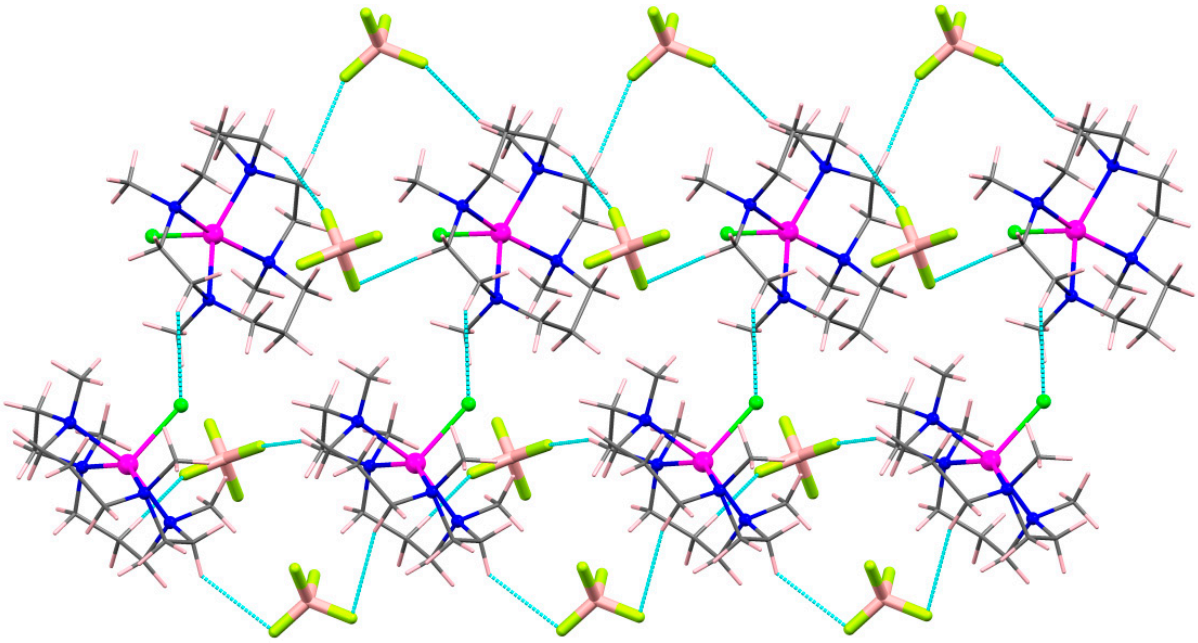


Figure S2. A view of supramolecular 2D arrangement of complex **1** through intermolecular H-bonding interactions.

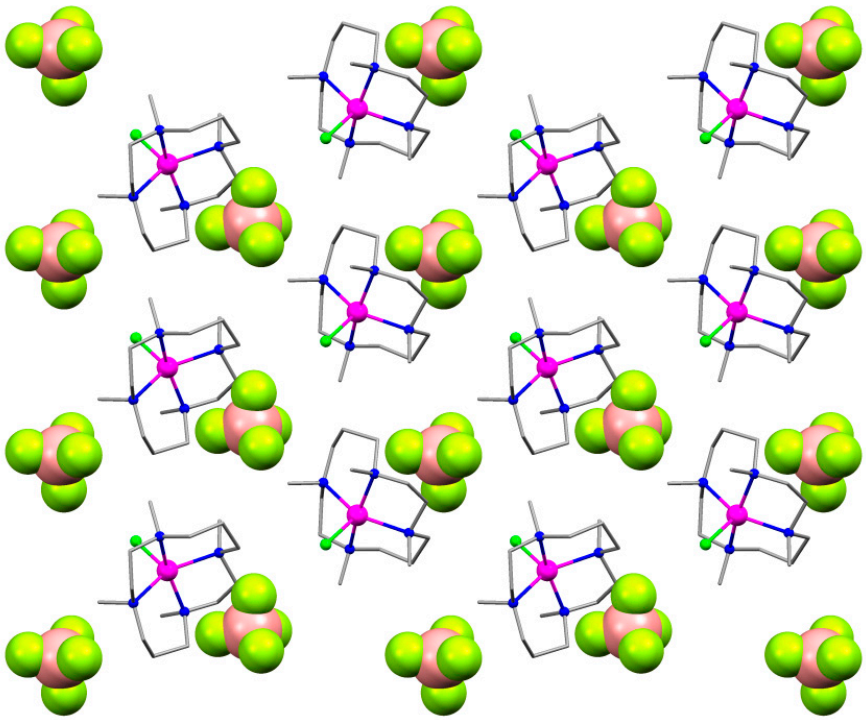


Figure S3. A view of packing diagram of complex **1** illustrating the continuous 2D arrangement of counter anions along the crystallographic *a*-axis.

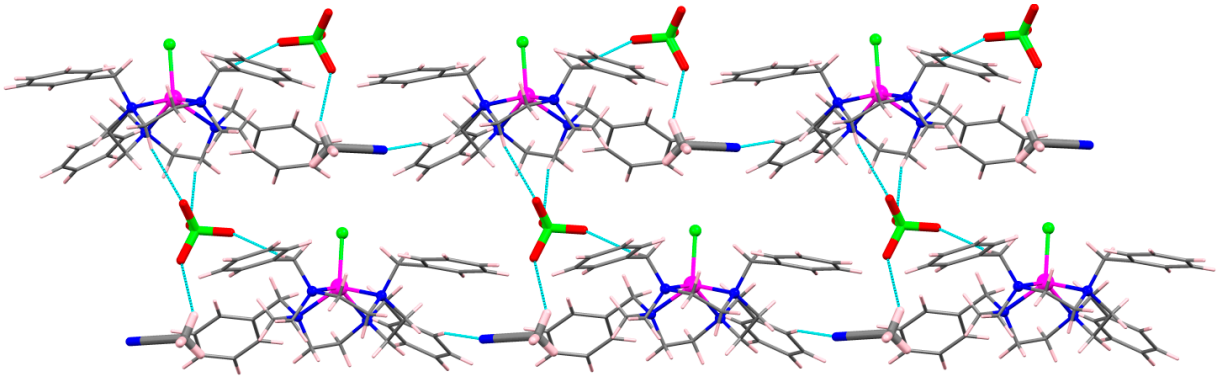


Figure S4. A view of supramolecular 2D arrangement of complex 2 through intermolecular H-bonding interactions.

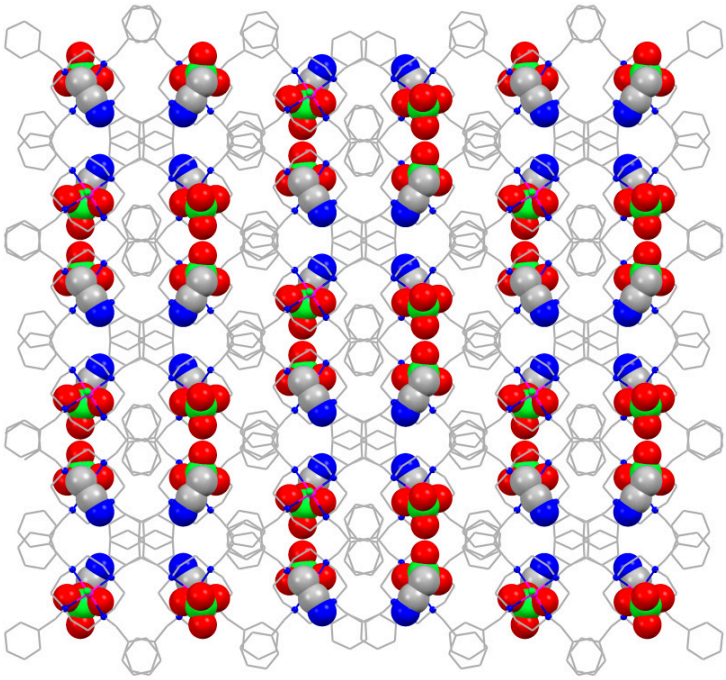


Figure S5. A view of packing diagram of complex **2** illustrating the continuous 2D arrangement of lattice solvent molecules and counter anions along the crystallographic *c*-axis.

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#
C6—H6A···Cl1	0.980	2.580	3.239	125.00	0
C1—H1B···F4	0.990	2.520	3.348	141.00	1
C9—H9B···F1	0.990	2.410	3.365	162.00	1
C8—H8B···Cl1	0.990	2.790	3.728	159.00	2
C10—H10A···F3	0.990	2.430	3.382	161.00	3
C14—H14B···F4	0.990	2.520	3.130	120.00	4

(0) x,y,z; (1) 1-x,1/2+y,1-z; (2) x,y,1+z; (3) -1+x,y,1+z; (4) 2-x,1/2+y,1-z.

Table S5. H-bond parameters found in complex **2.**

D– H···A	D–H(Å)	H···A(Å)	D···A (Å)	<D-H-A(°)	Symmetry#
C31—H31B···O1	0.990	2.440	3.305	146.00	0
C22—H22A···O4	0.990	2.570	3.530	163.00	1
C37—H37C···O3	0.980	2.500	3.316	140.00	1

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

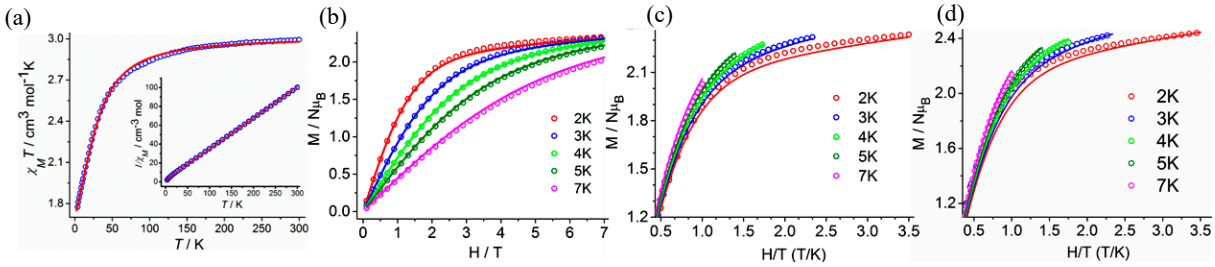


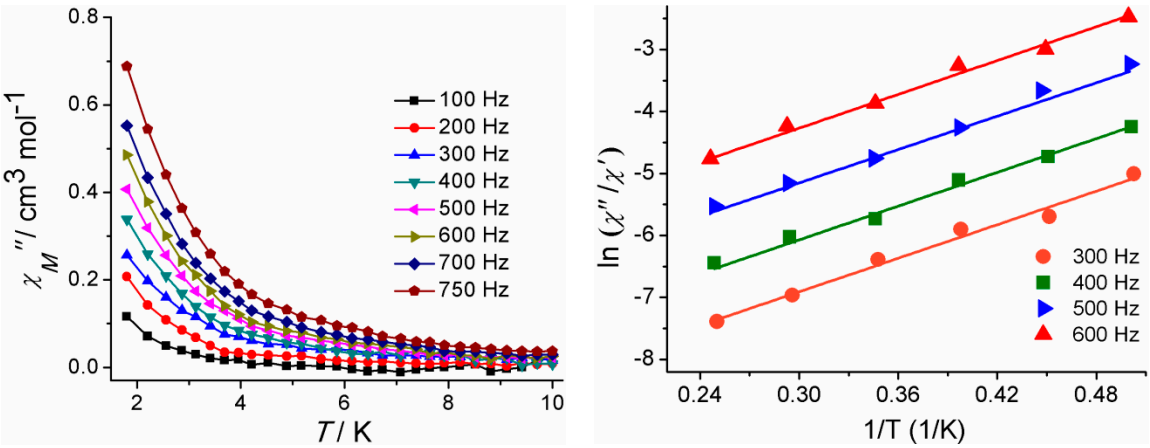
Figure S6. $\chi_M T$ *vs.* T plots measured at 0.1 T for complex **1** (**a**). $1/\chi_M$ *vs.* T plots shown in the inset; $M/N\mu_B$ *vs.* H plots for complex **1** (**b**) at the indicated temperatures. The solid lines are the best fit; $M/N\mu_B$ *vs.* H/T plots at the indicated temperatures for complexes **1** (**c**) and **2** (**d**). The solid lines are the best fit.

Table S6. Magnetic anisotropy (*D* parameter) and SIM parameters for previously reported pentacoordinate Co^{II} single ion magnets (SIMs).

Complex	Coordination geometry around Co^{II} center	*D* (cm^{-1})	U_{eff} (cm^{-1})	τ_0 (s)	Ref.
$[Co^{II}(tbta)N_3](ClO_4)$	Trigonal bipyramidal	−10.7	19.7	1.6×10^{-8}	1
$[Co^{II}(bzimpy)Cl_2]$	Trigonal bipyramidal	71.7	nr	nr	2
$[Co^{II}(Idppy)Cl_2]$	Trigonal bipyramidal	71.7	nr	nr	3
$[Co^{II}(ddppy)Cl_2]$	Trigonal bipyramidal	71.7	nr	nr	3
$[Co(phen)(DMSO)Cl_2]$	Trigonal bipyramidal	−17.0	10.4	5.6×10^{-9}	4
$[Co^{II}(Me_6tren)Cl](ClO_4)$	Trigonal bipyramidal	−6.2	nr	nr	5
$[Co^{II}(Me_6tren)Br](ClO_4)$	Trigonal bipyramidal	−2.5	nr	nr	5
$[Co(NS_3^{iPr})Cl](BPh_4)$	Trigonal bipyramidal	-23.0	32.0	2.1×10^{-11}	6
$[Co(NS_3^{tBu})Cl]ClO_4$	Trigonal bipyramidal	−21.4	21.0	4.6×10^{-8}	7
$[Co(NS_3^{tBu})Br]ClO_4$	Trigonal bipyramidal	−20.2	21.0	4.6×10^{-8}	7
$[Co(NS_3^{tBu})NCS]ClO_4$	Trigonal bipyramidal	−11.0	20.0	2.0×10^{-9}	7
$[Co^{II}(Me_4cyclam)N_3]ClO_4$	Trigonal bipyramidal	46.7	nr	nr	8
$[Co(TPMA)(CH_3CN)](BF_4)_2 \cdot CH_3CN$	Trigonal bipyramidal	9.66	15.0	1.7×10^{-8}	9
[Co(TPMA)Cl]Cl	Trigonal bipyramidal	−8.49	16.4	5.2×10^{-8}	9
[Co(TPMA)Br]Br	Trigonal bipyramidal	−7.18	12.3	8.0×10^{-8}	9
$[Co(tpa)Cl] \cdot ClO_4$	Trigonal bipyramidal	-10.1	12.0	7.2×10^{-6}	10
$[Co(tpa)Br] \cdot ClO_4$	Trigonal bipyramidal	-7.8	8.7	5.8×10^{-6}	10
$[Co(tbta)Cl] \cdot (ClO_4) \cdot (MeCN)_2 \cdot (H_2O)$	Trigonal bipyramidal	-7.5	8.1	3.5×10^{-6}	10
$[Co(tbta)Br] \cdot ClO_4$	Trigonal bipyramidal	-4.3	5.0	2.1×10^{-6}	10
$[Co^{II}(hdppy)Cl_2]$	Square pyramidal	151	9.4	1.3×10^{-7}	11
$[Co^{II}(DAPDPI)(NCS)_2]$	Square pyramidal	−40.5	11.1	3.6×10^{-6}	12
$[Co^{II}(DBPDPI)(NCS)_2]$	Square pyramidal	−40.6	16.6	5.1×10^{-7}	12
$[Co(bbp)Cl_2] \cdot (MeOH)$	Square pyramidal	14.9	19.6	5.8×10^{-5}	13
$[Co(bbp)Br_2] \cdot (MeOH)$	Square pyramidal	8.4	6.4	3.1×10^{-5}	13

$[Co(PP_3)Cl]\cdot ClO_4$	Square pyramidal	46.4	26.1	8.2×10^{-6}	14
$[Co(PP_3)Br]\cdot ClO_4$	Square pyramidal	40.7	23.9	6.7×10^{-6}	14
$[Co(14\text{-}TMC)Cl](BF_4)$ (**1**)	Square pyramidal	44.2	5.0	2.7×10^{-6}	This paper
$[Co(12\text{-}TBC)Cl](ClO_4)\cdot(MeCN)$ (**2**)	Square pyramidal	53.6	12.7	3.2×10^{-6}	This paper

nr = not reported.



(**a**) (**b**)

Figure S7. Temperature dependence of the out-of-phase (χ_M'') (**a**) AC magnetic susceptibility plots for complex **1** under 2000 Oe dc field; Natural logarithm of the ratio of χ_M'' over χ_M' *vs.* $1/T$ (**b**) for complex **1** (solid lines represent the best fit obtained from Equation (2) described in the main text).

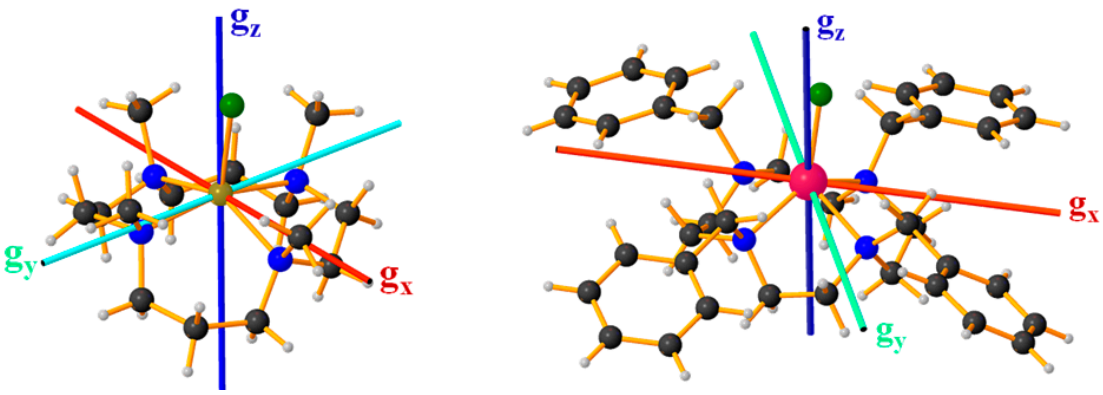


Figure S8. Orientation of the computed *g* tensor for complexes **1** (left) and **2** (right) with ORCA.

Table S7. 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			Complex 2		
		Energy	*D*	*E*	Energy	*D*	*E*
1st	4	1129	8.620	-6.926	768.3	47.398	40.233
2nd	4	2089	-2.392	0.221	1090.2	41.051	-30.688
3rd	4	2862	30.084	29.458	4116.3	1.825	1.712
4th	4	7278.2	8.422	-8.379	8311.1	-4.774	0.015
5th	4	9160.6	0.087	-0.087	8520.8	-0.631	-0.018
6th	4	10944.9	-0.077	0.008	10889.7	-6.708	0.017

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