Magnetic anisotropies and slow magnetic relaxation of three tetrahedral tetrakis(pseudohalido)-cobalt(II) complexes

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Electronic Supplementary Information

Table S1 Four-coordinate Co(II)-SIMs with the four identical donors

complexes	coodination core	D (cm^{-1})	U_{eff} (cm^{-1})	H_{dc}(kOe)	Ref.
$(Ph_4P)_2[Co(OPh)_4](CH_3CN)$	CoO_4	-11.1	21	1.4	S1
$K(Ph_4P)[Co(OPh)_4]$	CoO_4	-23.8	-	0	S1
$[Co^{II}Co^{III}_4L^1_2(\mu_{1,3}\text{-}O_2CCH_3)_2(\mu\text{-}OH)_2](ClO_4)_2{\cdot}4H_2O$	CoO_4	-31.31	-	3.0	S2
$[Co^{II}Co^{III}_4L^1_2(\mu_{1,3}\text{-}O_2CC_2H_5)_2(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)_4{\cdot}5H_2O$	CoO_4	-21.88	-	3.0	S2
$[Co^{II}Co^{III}_4L^2_2(\mu_{1,3}\text{-}O_2CCH_3)_2(\mu\text{-}OH)_2](ClO_4)_4{\cdot}H_2O$	CoO_4	-23.6	20.9	1.0	S3
$[Co^{II}Co^{III}_4L^2_2(\mu_{1,3}\text{-}O_2CC_2H_5)_2(\mu\text{-}OH)_2](ClO_4)_4{\cdot}H_2O$	CoO_4	-24.3	22.9	1.0	S3
$(Ph_4P)_2[Co(SPh)_4]$	CoS_4	-70	21	0	S4
$(Ph_4P)_2[Co(SPh)_4]$	CoS_4	-62	21	0	S1
$(K(18C6))_2[Co(C_3S_5)_2]$	CoS_4	-166	91	0	S5
$(Ph_4P)_2[Co(C_3S_5)_2]$	CoS_4	-161	33.9	0	S6
$(Bu_4N)_2[Co(C_3S_5)_2]$	CoS_4	-113.7	-	0	S7
$(Ph_4P)_2[Co(C_3S_5)_2]$	CoS_4	-116.4	-	0	S7
$(PPN)_2[Co(C_3S_5)_2]$	CoS_4	-105.7	-	0	S7
$(K(18C6))_2[Co(C_3S_5)_2]$	CoS_4	-118.0	91	0	S7
$(HNEt_3)_2[Co(L^3)_2]$	CoS_4	-71.6	26.8	1.0	S8
$[Co(L^4)_4](NO_3)_2$	CoS_4	-61.7	19.5	0	S9
$[Co(L^5)_4](ClO_4)_2$	CoS_4	-80.7	32.7	0	S9
$[Co(L^6)_4](ClO_4)_2$	CoS_4	-70.8	18.7	2.0	S9
$[Co(L^7)_4](ClO_4)_2$	CoS_4	-21.3	13.2	2.0	S9
$[Co(^iPr_2PSNPS^iPr_2)_2]$	CoS_4	-30.5	49	1.0	S10
$Co[(SPPh_2)_2N]_2$	CoS_4	-11.8	25.3	1.0	S11
$[Co(NH_2CSNH_2)_4](SiF_6)$	CoS_4	-5.1	34.8	0	S12
$(Ph_4P)_2[Co(SePh)_4]$	$CoSe_4$	-83	19	0	S1

$[Co(^{i}Pr_2PSeNPSe^{i}Pr_2)_2]$	$CoSe_4$	-30.4	-	1.0	S14
$Co[(SePPh_2)_2N]_2$	$CoSe_4$	-15.8	29.2	1.0	S15
$Co[(TeP^{i}Pr_2)_2N]_2$	$CoTe_4$	-45.1	22	0	S15
$(HNEt_3)_2[Co(dmps)_2]$	CoN_4	-115	118	0	S13
$(TTF)_2[Co(pdms)_2]$	CoN_4	-112	24.1	0	S14
$[Co((N^{t}Bu)_3SMe)_2]$	CoN_4	-58	75	0	S15
$[Co(dmbpy)_2](ClO_4)_2$	CoN_4	-57	73.9	2.5	S16
$(Bu_4N)_2[Co(L^8)_2]\cdot H_2O$	CoN_4	-130.8	58.4	0	S17
$(HNEt_3)_2[Co(L^9)_2]\cdot H_2O$	CoN_4	-144.1	46.0	0	S17
$K_2[Co(bmsab)_2]$	CoN_4	-118	-	0	S18
$(K\text{-}18C6)_2[Co(bmsab)_2]$	CoN_4	-130	-	0	S18
$(HNEt_3)_2[Co(btsab)_2]$	CoN_4	-110	-	0	S18
$[Co(cytosine)_2(NCS)_2]$	CoN_4	-6.1	13.0	1.0	S19
$[Co(cytosine)_2(NCO)_2]$	CoN_4	-7.4	19.1	1.0	S19
$[CoL^{10}_2](ClO_4)_2$	CoN_4	-45.9	46.9	1.0	S20
$[K(C_{12}H_{24}O_6)][Co(NCS)_4]$	CoN_4	+2.7	-	0.5	S21
$[Ba(C_{12}H_{24}O_6)\cdot 3H_2O][Co(NCS)_4]$	CoN_4	+5.2	-	2.0	S21
$(C_3N_2H_5)_2[CoCl_4]$	$CoCl_4$	-12.0	-	3.0	S22
$(C_{13}N_3H_{12})_2[CoCl_4]$	$CoCl_4$	12.1	-	4.0	S23

H_3L^1 = 2,6-bis((2-(2-hydroxyethylamino)-ethylimino)methyl)-4-methylphenol; H_3L^2 = (2,6-bis- [{2-(2-hydroxyethylthio)ethylimino}methyl]-4-methylphenol;H_2L^3 = 1,2-dithiol-o-carborane; L^4 = thiourea; L^5 = 1,3-*n*-butylthiourea; L^6 = 1,3-phenylethylthiourea; L^7 = 1,1,3,3-tetramethylthiourea; H_2pdms = 1,2-bis(methanesulfonamido) benzene; dmbpy = 6,6'-dimethyl-2,2'-bipyridine; H_2L^8 = N,N′-diphenyloxamide; H_2L^9 = N,N′-bis(p-toluenesulfony1) oxamide; TTF = tetrathiafulvalene; bmsab = 1,2-bis(methanesulfonamido)benzene; btsab = 1,2-bis-(toluenesulfonamido)benzene; L^{10} = 2,9-diphenyl-1,10-phenanthroline.

Table S2 The deviation parameters of $[Co(N_3)_4]^{2-}$ anions relative to the ideal tetrahedron calculated by the continuous shape measure analyses

Refcode	CCDC number	Deviation parameters	Ref.
COSROU	880824	0.107	S24
FOCLEQ	986657	0.122	S25
Complex **1**	2024569	0.399, 0.960[a]	This work

[a]One azido ligand is disordered in two positions, therefore two values of deviation parameter were obtained for **1**.

Table S3 The deviation parameters of $[Co(NCO)_4]^{2-}$ anions relative to the ideal tetrahedron calculated by the continuous shape measure analyses

Refcode	CCDC number	Deviation parameters	Ref.	Refcode	CCDC number	Deviation parameters	Ref.
CASWUR	863951	0.136	S26	CASXEC	858779	0.044	S26
CASXAY	863950	0.022	S26	CASXIG	858570	0.161	S26
CASXOM	868569	0.074	S26	CASXUS	858568	0.016	S26
DAYFAN	1529486	0.184	S27	FOPLIG	636957	0.137	S28
SIQHIM	1566120	0.126	S29	SOTVEC	CSD 55434	0.041,0.030	S30
TECNOH	1543050	0.033	S31	YIWTIK	1888082	0.041,0.033	S32
Complex **2**	1945219	0.073	This work				

Table S4 The deviation parameters of $[Co(NCS)_4]^{2-}$ anions relative to the ideal tetrahedron calculated by the continuous shape measure analyses

Refcode	CCDC number	Deviation parameters	Ref.	Refcode	CCDC number	Deviation parameters	Ref.
ACIMIK	836768	0.085	S33	BEYZOU	1109765	0.059	S34
BEZPUR	1109841	0.491	S35	BEZQEC	1109842	1.003	S35
BEZQEC01	1109843	0.137	S35	BEZQEC02	631772	0.395	S36
BEZQEC03	631773	0.403	S36	BEZQEC04	631774	0.333	S36
CASBUT	1120514	0.132	S37	CEQRUO	1484386	0.042	S38
CEQRUO01	1484383	0.033	S38	CEQSEZ	1484385	1.506	S38
CEQSID	1484384	1.343	S38	CILDUW	—	0.084	S39
COCRYP	1128244	a	S40	COKHAL	1129056	0.108	S41
COKHAL01	1129057	a	S42	DUPYUJ	766681	0.400	S43
DAYDUF	1529275	0.102	S27	DEBQOS	882765	0.649	S44
DEDFUN	1137871	0.056	S45	DEDFUN10	1137872	0.055	S46
DEDFUN11	1498514	0.036	S21	DOHGEN	666225	0.155,0.134	S47
EBECIZ	807031	0.149	S48	ENICON	1149758	0.294	S49
FAXLAR	1153166	0.056	S50	FUGLID	754141	0.703,0.358	S51
FEXGUN	1526142	0.163	S52	FOCLIU	986658	0.380,0.124	S25
FOQFOH	686545	0.039	S53	FOQFIB	686544	0.359	S53
FOHMOF	274583	0.313	S54	GAZKIB	1164762	0.255	S55
GULBEW	1050961	0.314	S56	HECVET	1480986	0.167	S57
HGTCOT	1175838	2.352	S58	HOKTIM	870983	0.054	S59
HORLIJ	102666	0.088	S60	HOSNUA	1017350	0.090	S61
HOTCIE	1017349	0.082	S61	IJECOP	167818	0.053	S62
JAJWID	1498515	0.101	S21	JAHBEC	1429634	0.154	S63
KAGRUH	743433	0.286	S64	KAGSAO	743435	0.042	S64
KESHEX	800175	0.156	S65	KAYSUA	851712	0.207,0.050	S66
KIPMEE	1854179	0.052	S67	KESHIB	800176	0.056	S65

KIPMII	1854180	0.612	S67	KOYQUM	1023601	0.122	S68
KOYQOG	1023600	0.097	S68	KUNRUG	—	0.191	S69
KUBKAV	991212	0.209	S70	LAYKAZ	714550	0.186,0.219	S71
LAFKIO	—	0.039	S72	MAYXEQ	279772	0.092,0.111	S73
MENBAI	148584	0.065	S74	MENBAI01	829599	0.075	S75
NESNAC	874866	0.044	S76	NERNIH	171301	0.408	S77
ORUBIP	2002739	0.118	S78	NURROI	648268	0.092,0.152	S79
OXEROA	702325	0.188	S80	OMUXIG	2039818	0.042,0.053	S81
PABQAN	1037196	0.053	S82	PABPUG	1037195	0.098	S82
PATZOL	1228720	0.086	S83	PANDUD	—	0.070,0.071	S84
PEJJEU	613965	0.262	S85	PAZBUQ	1480787	0.242	S86
PODZIU	1859673	0.145	S87	PELJAR	1230610	0.360	S88
QACWEY	745552	0.117	S89	QACWAU	744652	0.105	S89
QAYTAL	153372	0.024	S90	QAWDEZ	846920	0.090	S91
QITSUJ	800156	0.028	S92	QITSOD	800157	0.102	S92
QUXKOK	786428	0.057	S93	QQQBFD01	945401	1.378,0.315	S94
QQQBFD	—	a	S95	RANPOO	768800	0.615	S96
ROQDOQ	402939	0.168	S97	RUDTUG	754076	0.046	S98
SERKOS	1563305	0.270	S99	SIQHEI	1566119	0.080	S100
SOHKIJ	—	0.048	S101	SIZZAF	1872737	0.115,0.138	S102
TECNIB	1543049	0.119	S31	TEGGES	281767	0.253	S103
TEXRIZ	855726	0.238	S104	TUXQEI	187685	0.065	S105
VAKKIB	—	0.130	S106	VALBEP	1279535	0.147	S107
VAWXAU	820990	0.073	S108	VIZYOU	985959	0.036	S109
VALBEP10	1279536	a	S110	WUYSAM	1431752	0.067	S111
WODZAT	1874233	0.181	S112	XEDSOO	153585	0.077	S113
XEDSEE	153583	0.092	S113	XUBTAR	1008750	0.160	S114
XIXQUT	1831626	0.090	S115	YEDBER	1457909	0.172	S116
YEDBAN	1457908	0.136	S116	YEFBOD	941188	0.934	S116

YEJGOM01	1551780	0.199	S117	YEJGOM	1551779	0.210	S117
YIWTAC	1888080	0.170	S32	YEPHIK	400837	0.086	S118
ZIFKAA01	1312259	a	S35	ZIFKAA	1312258	0.192	S119
Complex **3**	1945220	0.055	This work				

a. The deviation parameters cannot be calculated as the atom coordinates are not available.

Table S5 Summary of crystal data and refinement for **1-3**

	1	**2**	**3**
Empirical formula	$C_{48}H_{40}CoN_{12}P_2$	$C_{52}H_{40}CoN_4P_2O_4$	$C_{52}H_{40}CoN_4P_2S_4$
Formula weight, g·mol^{-1}	905.79	905.75	969.99
T, K	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c	C2/c
a, Å	14.2921(7)	22.276(3)	22.538(3)
b, Å	21.5474(9)	14.828(3)	15.0939(18)
c, Å	15.6029(7)	13.6901(18)	14.9601(18)
β, deg	94.754(2)	104.641(4)	108.721(2)
V, Å^3	4788.5(4)	4375.1(11)	4820.0(10)
Z	4	4	4
D_c, g•cm^{-3}	1.256	1.375	1.337
F(000)	1876	1876	2004
Absorption Coefficient,mm^{-1}	0.471	0.518	0.636
Crystal size, mm	0.35 × 0.32 × 0.30	0.22 × 0.20 × 0.16	0.22 × 0.16 × 0.14
θ range for data collection	2.017 – 25.999	2.100- 27.518	1.65 2- 27.491
Index ranges	-17 ≤ h ≤ 17 -26 ≤ k ≤ 26 -19 ≤ l ≤ 17	-28 ≤ h ≤ 26 -19 ≤ k ≤ 15 -15 ≤ l ≤ 17	-29 ≤ h ≤ 25 -8 ≤ k ≤ 19 -18 ≤ l ≤ 19
reflection collected	39843	18416	11605
independent refledtions	9401 (R_{int} = 0.0431)	5037 (R_{int} = 0.0793)	5410 (R_{int} = 0.0274)
data/restraints/parameters	9401/43/604	5037/0/285	5410/0/285
completeness	0.999	0.999	0.986
goodness-of-fit on F^2	1.014	1.098	1.037
final *R* indices [$I \geq 2\sigma(I)$]	R_1 = 0.0566, wR_2 = 0.1248	R_1 = 0.0570, wR_2 = 0.1204	R_1 = 0.0458, wR_2 = 0.1177
R indices (all data)	R_1 = 0.0912, wR_2 = 0.1406	R_1 = 0.0757, wR_2 = 0.1269	R_1 = 0.0637, wR_2 = 0.1318
largest diff. peak and hole	0.784 and -0.799	0.683 and -0.409	0.325 and -0.604
CCDC No.	2024569	1945219	1945220

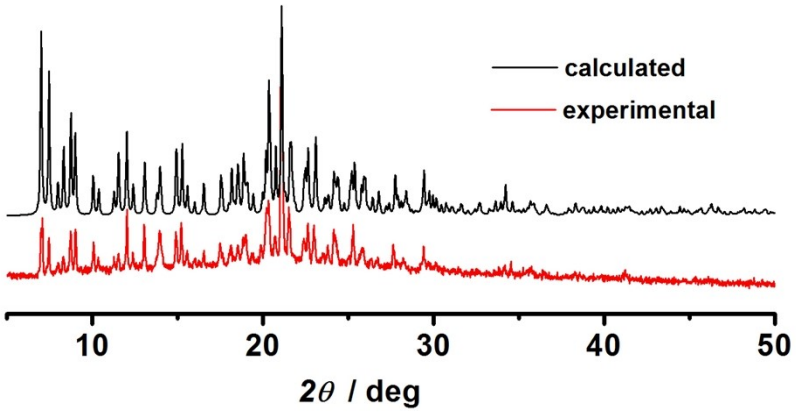


Fig. S1 XRD patterns for **1**.

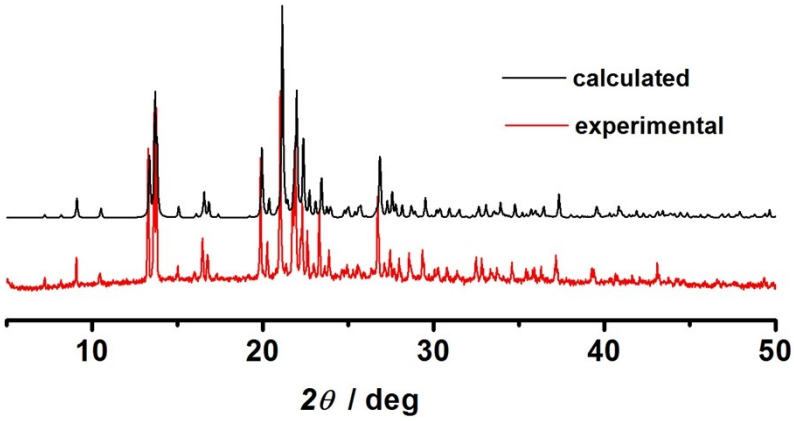


Fig. S2 XRD patterns for **2**.

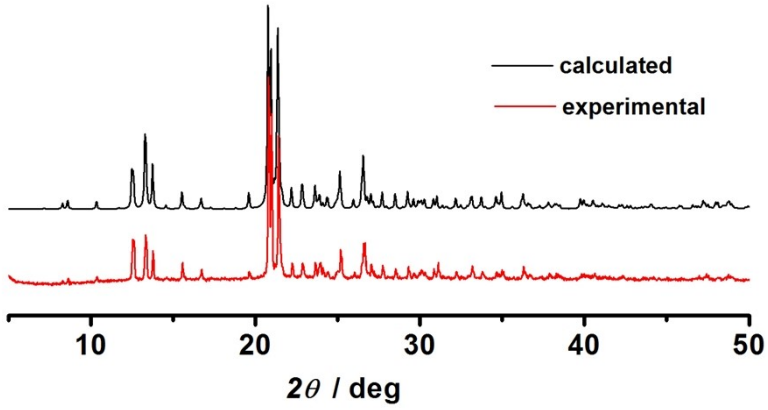
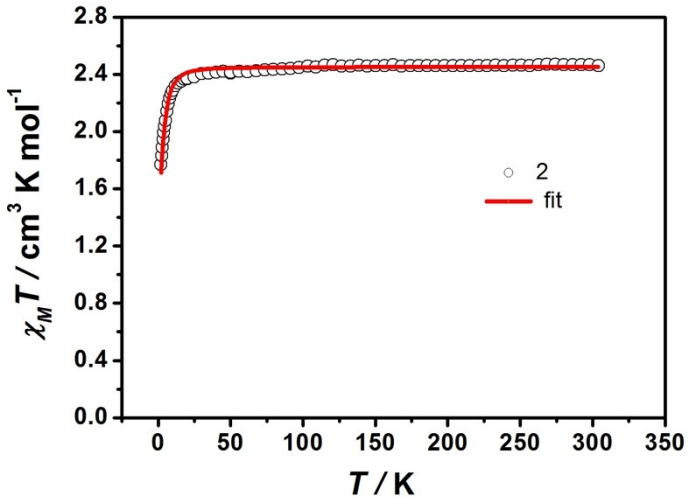
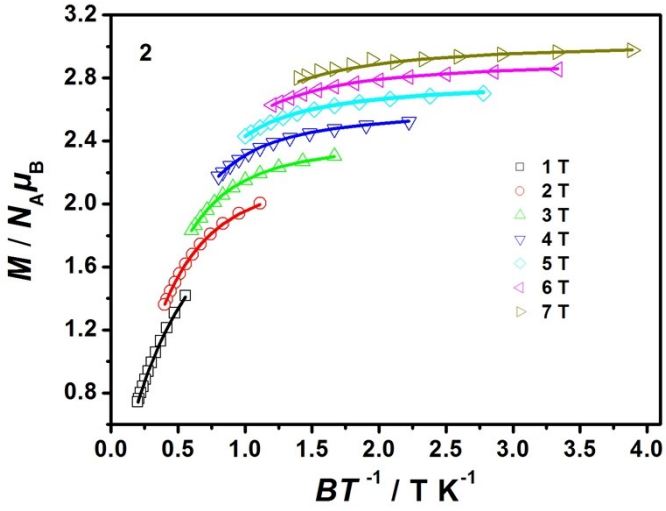


Fig. S3 XRD patterns for **3**.

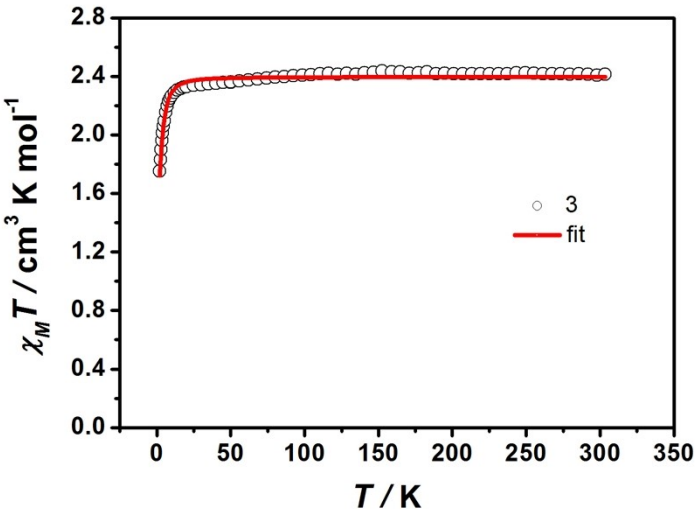


(a)

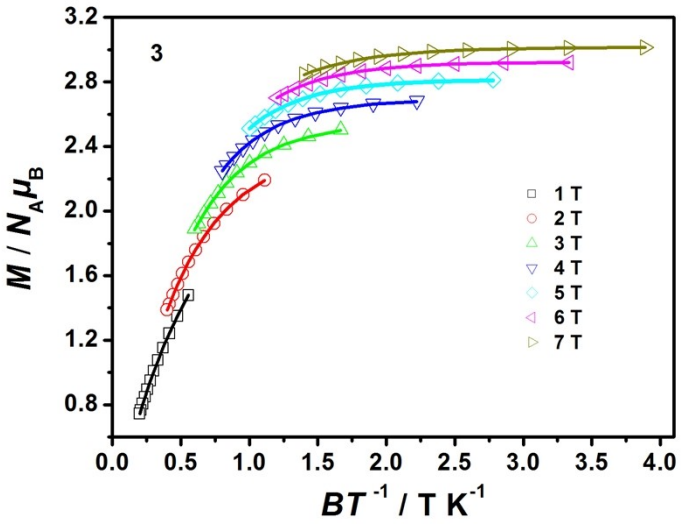


(b)

Fig. S4 (a)Variable-temperature dc susceptibilities and (b) variable- temperature, variable -field dc magnetization data of **2**. Fields of 1-7 T were used at temperatures from 1.8 K to 5.0 K. Solid lines are the fits with the *PHI* program



(a)



(b)

Fig. S5 Variable-temperature dc susceptibilities and variable- temperature, variable-field dc magnetization data of **3**. Fields of 1-7 T were used at temperatures from 1.8 K to 5.0 K. Solid lines indicate the fits with the *PHI* program.

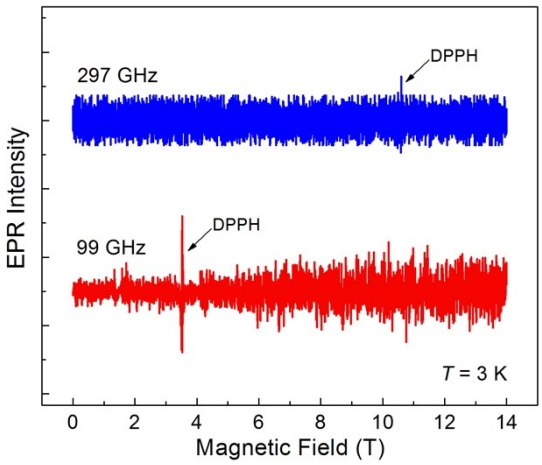
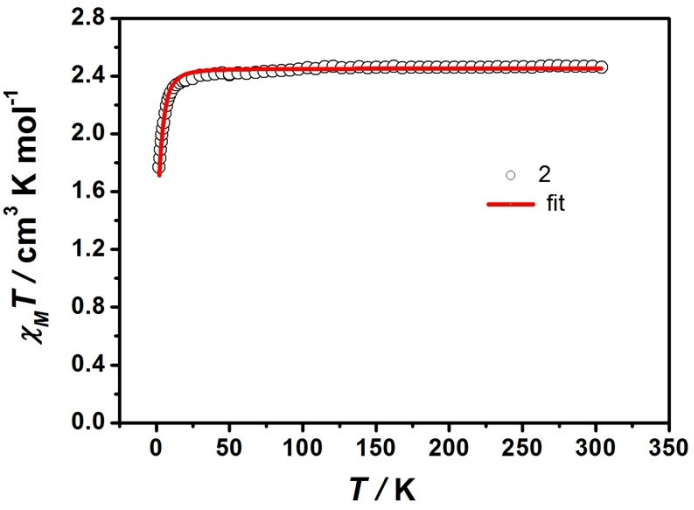
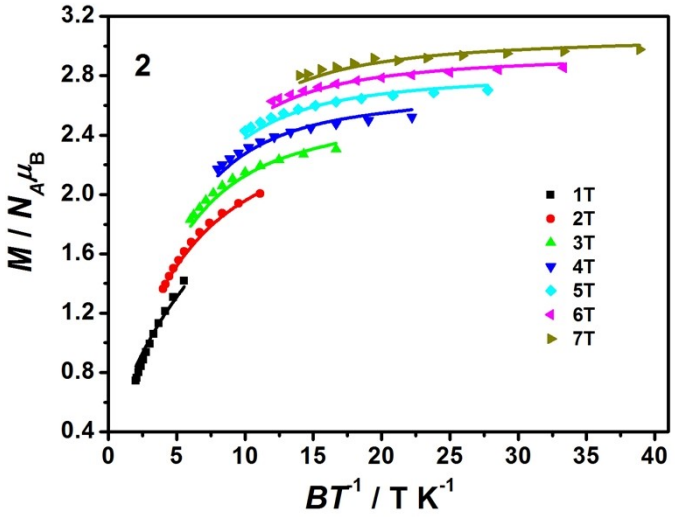


Fig. S6 The experimental HFEPR spectra in derivative mode for **1** under 99 and 297 GHz at 3 K.

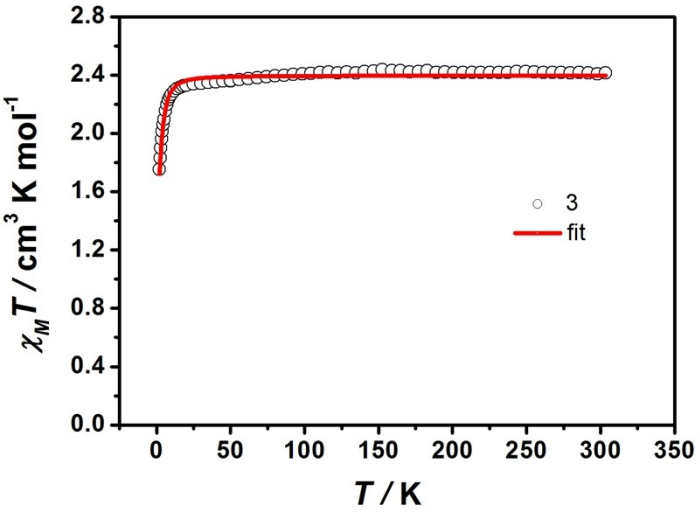


(a)

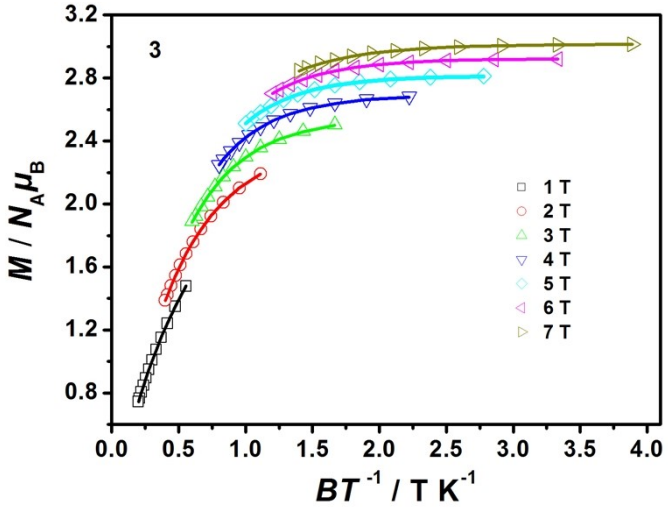


(b)

Fig. **S7** (a) Variable-temperature dc susceptibility under an applied dc field of 0.1 T for **2**. (b) Variable-temperature, variable-field dc magnetization data of **2**. Fields of 1-7 T were used at temperatures from 1.8 K to 5.0 K. Solid lines are the simulated curves using the parameters from HFEPR spectra with *PHI* program.



(a)



(b)

Fig. **S8** (a) Variable-temperature dc susceptibility under an applied dc field of 0.1 T for **3**. (b) Variable-temperature, variable-field dc magnetization data of **3**. Fields of 1-7 T were used at temperatures from 1.8 K to 5.0 K. Solid lines are the simulated curves using the parameters from HFEPR spectra with *PHI* program.

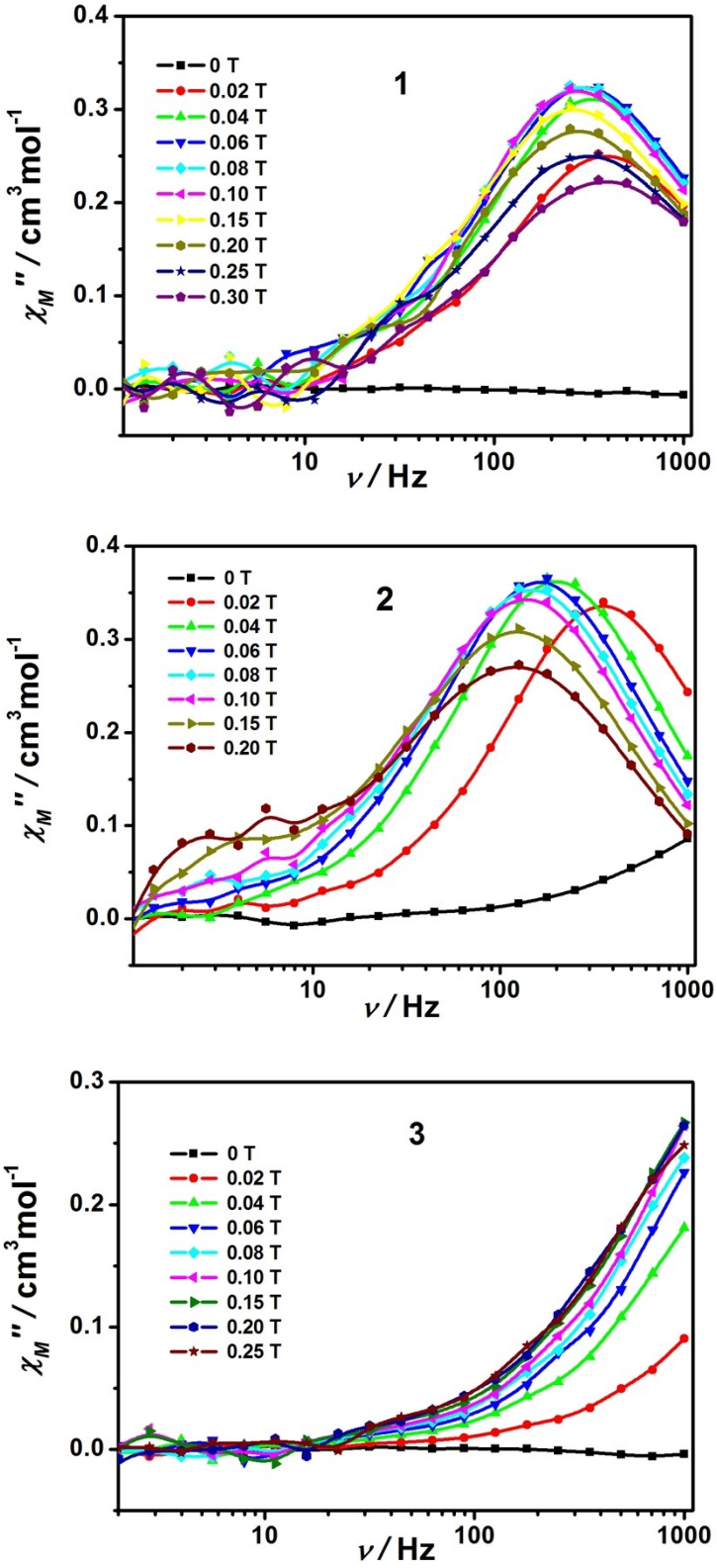
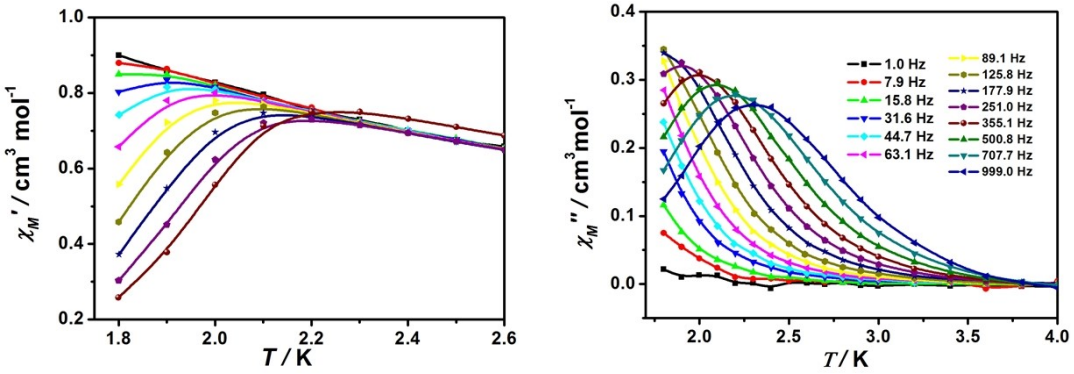
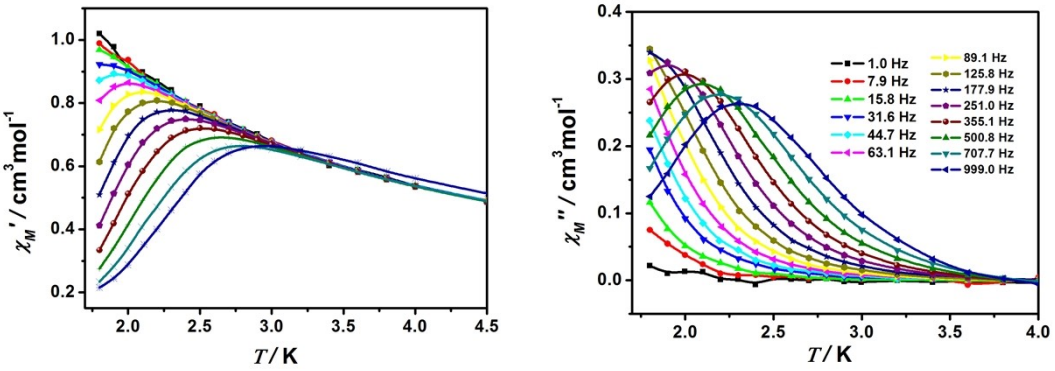


Fig. S9 Frequency dependence of out-of-phase (χ_M'') ac susceptibility at 1.8 K under the different applied static fields (from 0.02 to 0.30 T for **1**, 0 to 0.20 T for **2**, 0 to 0.25 T for **3**). The solid lines are for eye guide.



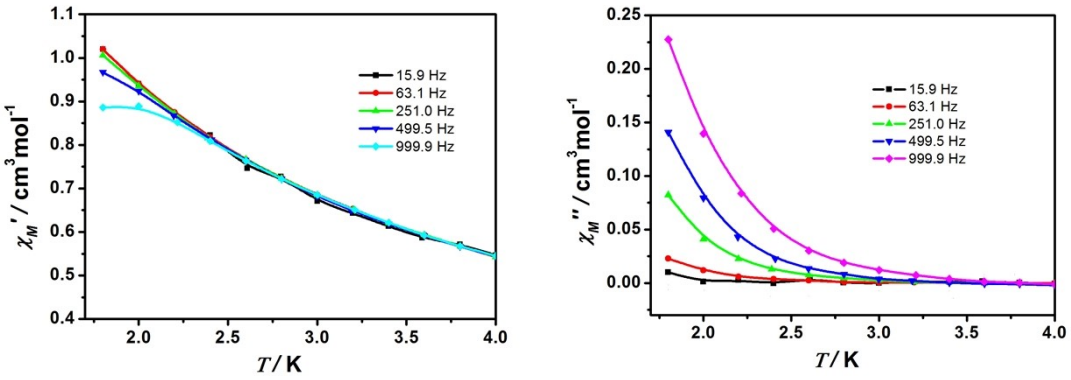
(a) (b)

Fig. S10 (a) Temperature dependence of in-of-phase (χ_M') and (b) out-of-phase ac susceptibility (χ_M'') at different ac frequency under a 0.08 T dc field for **1**. The solid lines are for eye guide.



(a) (b)

Fig. S11 (a) Temperature dependence of in-of-phase (χ_M') and (b) out-of-phase ac susceptibility (χ_M'') at different ac frequency under a 0.1 T dc field for **2**. The solid lines are for eye guide.



(a) (b)

Fig. S12 (a) Temperature dependence of in-of-phase (χ_M') and (b) out-of-phase ac susceptibility (χ_M'') at different ac frequency under a 0.1 T dc field for **3**. The solid lines are for eye guide.

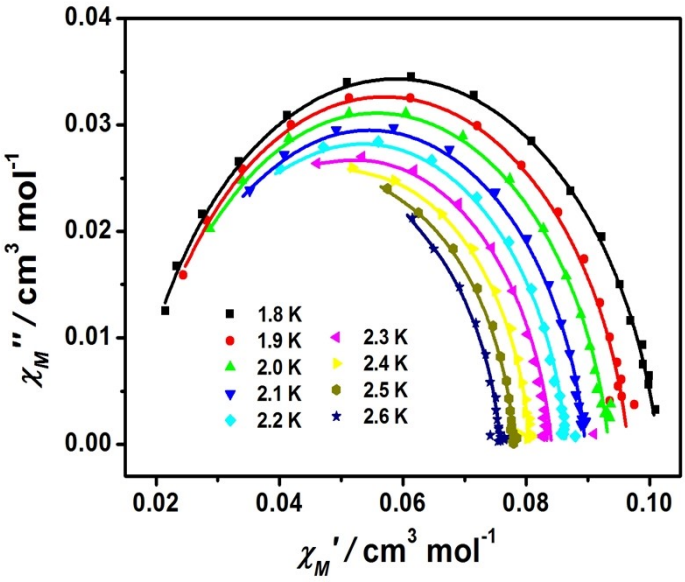


Fig. S13 Cole-Cole plot obtained from the ac susceptibility data under 0.1 T dc field between 1.8 and 2.6 K for **2**. Solid lines represent the best fits to a generalized Debye model.

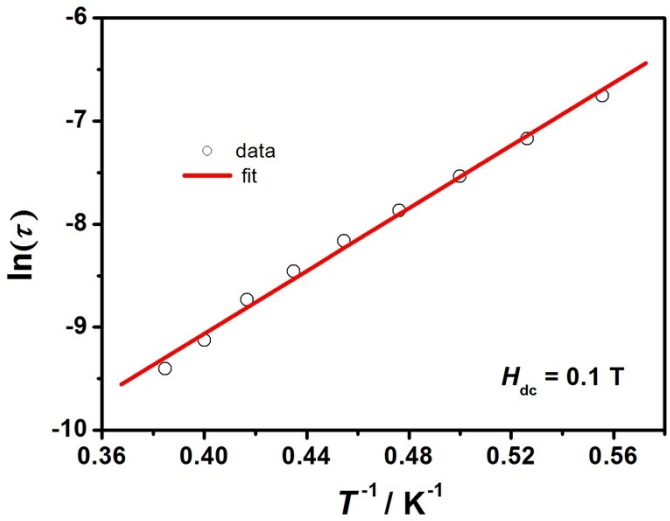


Fig. S14 Arrhenius plot for **2**. The solid lines represent the best fit to the data.

Table S6 The parameters obtained by fitting the Cole-Cole plot under 0.1 T for **2**

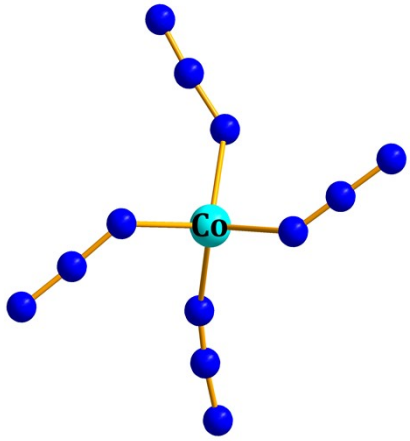
T (K)	χ_S	χ_T	τ	α	*Resi.*
1.8	0.01639	0.10132	0.00117	0.126789	1.01607×10^{-5}
1.9	0.01755	0.0965	7.69861×10^{-4}	0.111988	2.29077×10^{-5}
2.0	0.01821	0.09336	5.34053×10^{-4}	0.111203	7.74388×10^{-6}
2.1	0.01968	0.08955	3.81892×10^{-4}	0.0984098	6.82749×10^{-6}
2.2	0.02057	0.08646	2.84396×10^{-4}	0.0892374	5.50196×10^{-6}
2.3	0.02103	0.08407	2.11807×10^{-4}	0.0963511	5.74912×10^{-5}
2.4	0.02288	0.08055	1.62964×10^{-4}	0.0695094	4.48526×10^{-6}
2.5	0.02149	0.07806	1.18931×10^{-4}	0.0781255	3.58249×10^{-6}
2.6	0.01842	0.0758	8.34813×10^{-5}	0.0893209	6.94129×10^{-6}

Ab initio calculation

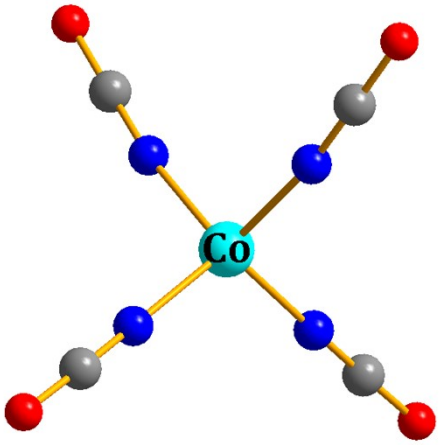
Complete-active-space self-consistent field (CASSCF) calculations with MOLCAS 8.2[S120] program package were performed on **1**−**3** (see Fig. S15 for the calculated complete structures of **1**−**3**) on the basis of X-ray determined geometries.

The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for Co(II); VTZ for close N atoms; VDZ for distant atoms. The calculations employed the second-order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set. The active electrons in 10 active orbitals considering the 3d-double shell effect (5+5′) include all seven 3d electrons (CAS(7 in 5+5′) for Co(II)), and the mixed spin-free states are 50 (all from 10 quadruplets and all from 40 doublets for Co(II)). And then, the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure.[S121–S122] SINGLE_ANISO[S123–S125] program was used to obtain the spin-free energies, spin-orbit energies, parameters *D(E)* (cm^{-1}), ***g*** tensors, magnetic axes etc. based on the above CASSCF/RASSI-SO calculations.

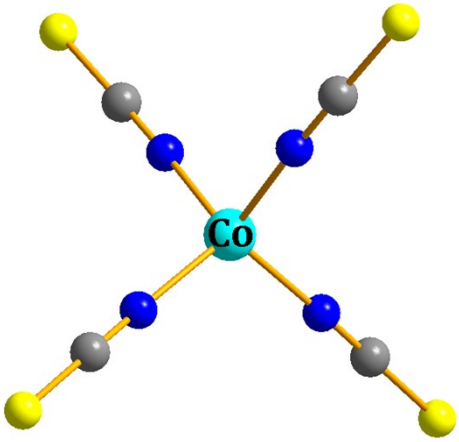
To deeply analyze the magnetic anisotropies, ORCA 4.2 calculations[S126] were performed with complete active space self-consistent field calculations (CASSCF), followed by N-electron valence second-order perturbation theory (NEVPT2). The spin-orbit coupling (SOC) operator used was the efficient implementation of the multicenter spin-orbit mean-field (SOMF) concept developed by Hess et al.[S127] The NEVPT2[S128–S131] calculation with seven 3d electrons in five Co 3d-based orbitals (CAS(7, 5)). In the calculations, the orbitals were determined for the average of 10 $S = 3/2$ and 40 $S = 1/2$ roots. All calculations were performed with triple-ζ with one polarization function def2-TZVP[S132–S134] basis set for all atoms.



1



2



3

Fig. S15 Calculated complete structures of **1**−**3**.

Table S7. Calculated spin-free energies (cm^{-1}) of the lowest ten terms (S = 3/2) of **1**−**3** using CASSCF/ RASSI-SO with MOLCAS 8.2.

	1	**2**	**3**
	E/cm^{-1}	E/cm^{-1}	E/cm^{-1}
1	0.0	0.0	0.0
2	3370.6	4057.6	4468.1
3	4184.3	4098.4	4627.4
4	4566.7	4370.7	4724.1
5	6479.0	6975.7	7603.0
6	7247.4	7177.8	8036.4
7	7367.2	7624.2	8311.1
8	20442.4	20864.6	21492.6
9	20877.6	21355.4	21563.1
10	21378.3	21500.6	21918.6

Table S8 Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of **1**−**3** using CASSCF/RASSI-SO with MOLCAS 8.2.

	Spin-orbit states	Energy (cm^{-1})	Spin-free states, Spin, Weights				
1	1	0.0	1,1.5,0.9713	2,1.5,0.0191	3,1.5,0.0049	4,1.5,0.0033	18,0.5,0.0005
	2	14.5	1,1.5,0.9779	3,1.5,0.0091	4,1.5,0.0089	2,1.5,0.0028	17,0.5,0.0006
2	1	0.0	1,1.5,0.9759	2,1.5,0.0119	3,1.5,0.0068	4,1.5,0.0041	17,0.5,0.0005
	2	6.9	1,1.5, 0.9775	4,1.5,0.0093	3,1.5,0.0080	2,1.5,0.0040	18,0.5,0.0006
3	1	0.0	1,1.5,0.9803	2,1.5,0.0089	4,1.5,0.0077	3,1.5, 0.0020	17,0.5,0.0007
	2	4.0	1,1.5,0.9810	3,1.5,0.0096	4,1.5,0.0043	2,1.5,0.0040	18,0.5,0.0005

Table S9. Contributions of the excited states (with relative energy cm^{-1}) to *D* values (cm^{-1}) for complexes **1**−**3** using NEVPT2 with ORCA 4.2.

Complexes	State No.	Mult	Energy, cm^{-1}	Contribution, cm^{-1}
				D
1	1	4	6330.6	−13.1
	2	4	8187.4	3.7
2	1	4	3886.4	−15.3
	3	4	4180.3	11.6
3	1	4	4282.8	11.2
	2	4	4423.2	−15.7
	3	4	4519.7	6.3

Table S10. Relative energies (cm^{-1}) of ligand field one-electron states (in the basis of *d*-AOs) of **1**−**3** from AILFT analysis using NEVPT2 with ORCA 4.2.

Complexes	No.	LF one-electron state	Energy, cm^{-1}
1	1	$0.99\ d_{x^2-y^2} - 0.14\ d_{yz}$	0.0
	2	$-0.98\ d_{z^2} + 0.19\ d_{xz}$	73888.6
	3	$-0.98\ d_{yz} - 0.15\ d_{x^2-y^2}$	78202.4
	4	$-0.98\ d_{xz} - 0.19\ d_{z^2}$	78630.6
	5	$-0.99\ d_{xy} - 0.14\ d_{yz}$	83235.0
2	1	$0.81\ d_{x^2-y^2} + 0.59\ d_{z^2}$	0.0
	2	$1.00\ d_{xz}$	126.8
	3	$0.97\ d_{xy} + 0.23\ d_{yz}$	3959.3
	4	$0.97\ d_{yz} - 0.23\ d_{xy}$	4010.2
	5	$0.81 d_{z^2} - 0.59\ d_{x^2-y^2}$	4351.3
3	1	$0.96\ d_{xz} + 0.21\ d_{z^2} - 0.19\ d_{yz}$	0.0
	2	$-0.76\ d_{x^2-y^2} - 0.54\ d_{z^2} + 0.31\ d_{xy}$	69.3
	3	$-0.81\ d_{z^2} + 0.52\ d_{x^2-y^2} - 0.23 d_{xy}$	4318.1
	4	$-0.89 d_{xy} - 0.28\ d_{yz} - 0.37\ d_{x^2-y^2}$	4451.3
	5	$-0.94\ d_{yz} + 0.26\ d_{xy} - 0.19\ d_{xz}$	4659.6

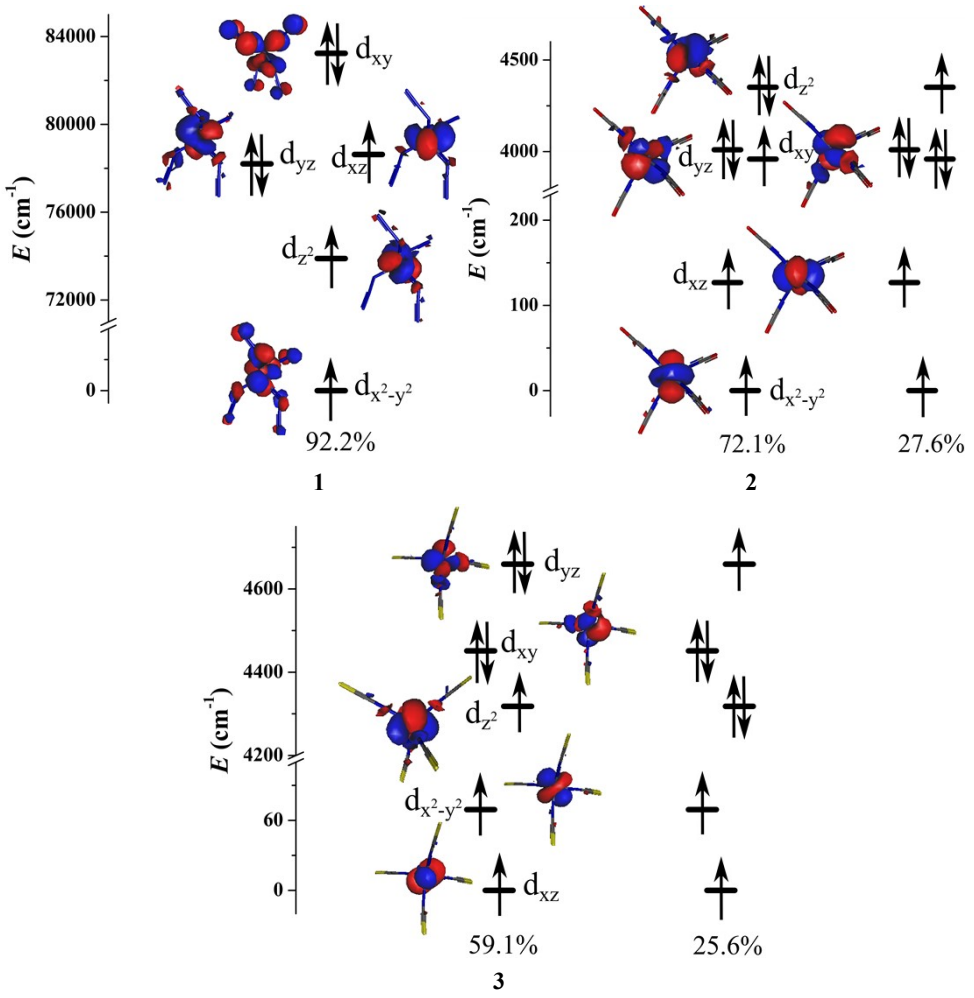


Fig. S16 Orbital energies computed for the ground state of **1**−**3** using NEVPT2 with ORCA 4.2. The percentage refers to the percent of the corresponding configuration mixing.

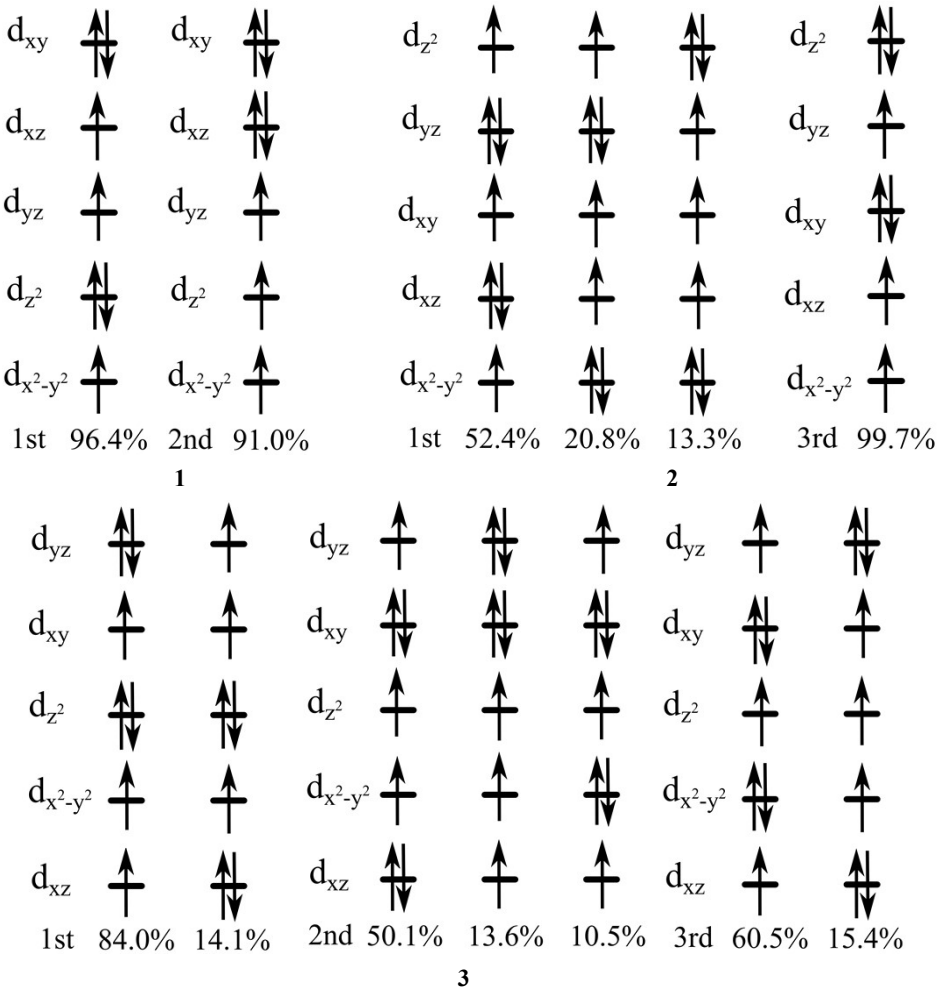


Fig. S17 Orbital energies computed for the selected excited states of **1**−**3** using NEVPT2 with ORCA 4.2. The computed CI coefficients larger than 10% are shown above.

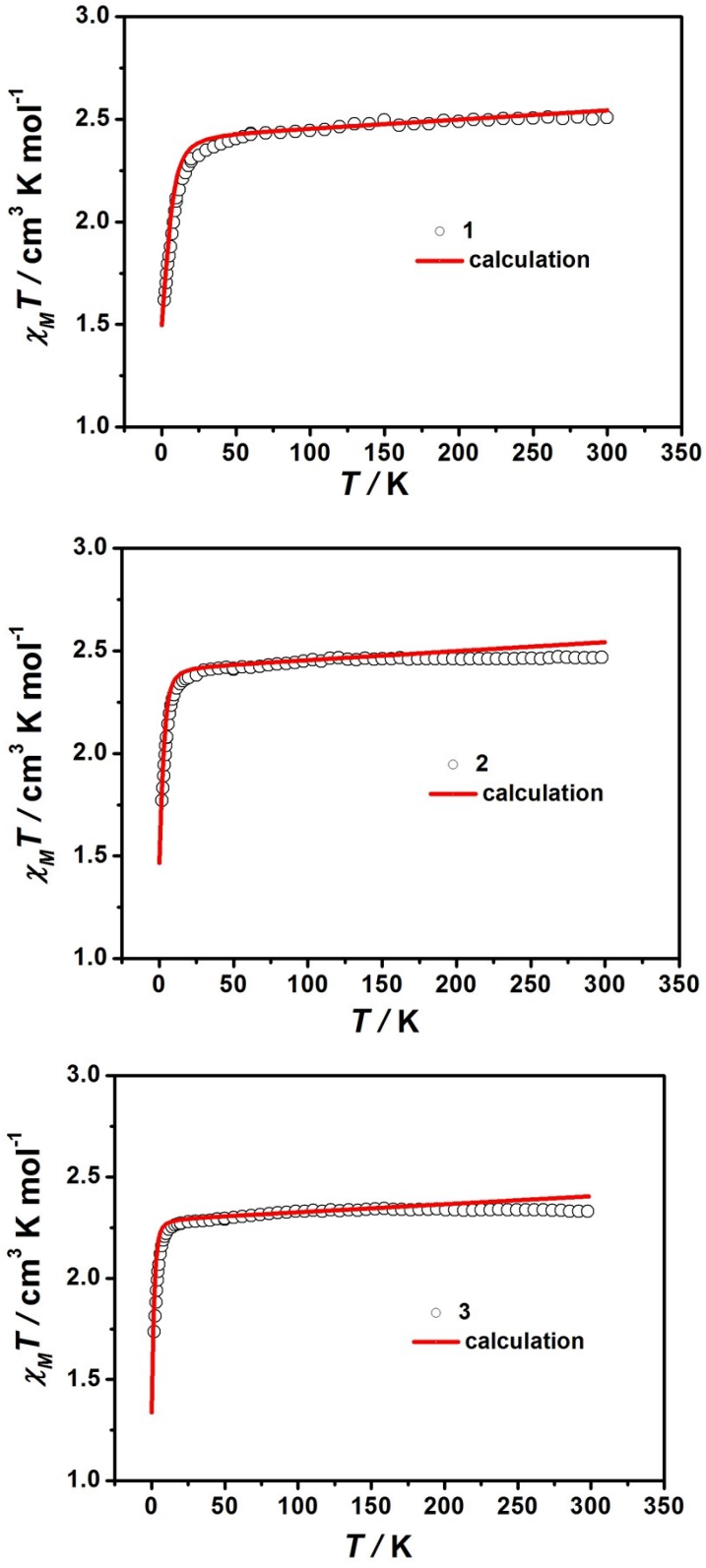
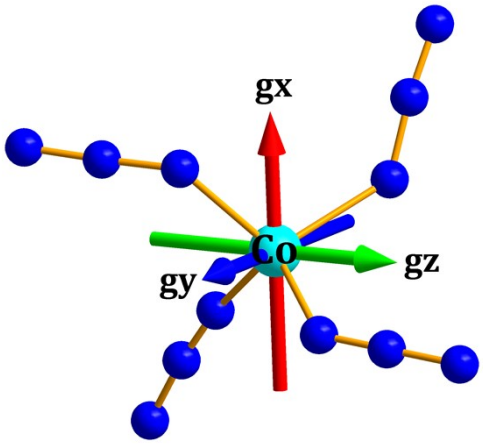
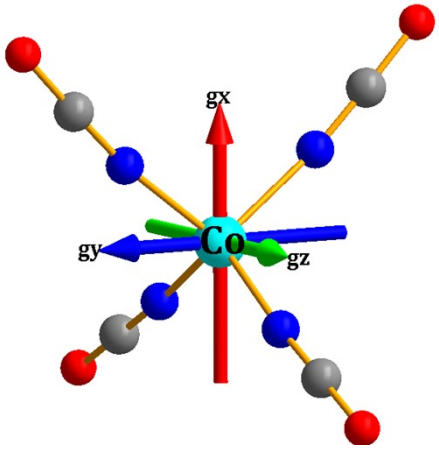


Fig. S18 Calculated (red solid line) data of magnetic susceptibilities of **1**–**3**.



1



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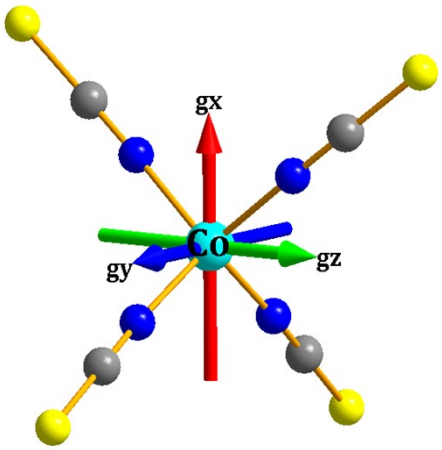

3

Fig. S19 Orientations of the local magnetic axes (red: g_x; blue: g_y; green: g_z) of the ground spin-orbit states on Co(II) ions in **1**-**3**.

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