Influence of Counter-Anion on the Zero Field Splitting of Tetrahedral Co(II) Thiourea Complexes

Shalini Tripathi[‡,#] Shefali Vaidya[‡,#] , Kamal Uddin Ansari[#], Naushad Ahmed[#], Eric Rivière[⊥], Lena Spillecke,[†] Changhyun Koo,[†] Rüdiger Klingeler,[†,+] Talal Mallah[⊥]*, Gopalan Rajaraman[#]* and Maheswaran Shanmugam[#]*

[‡] Authors contributed equally.

[#] Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, India.

[†] Kirchhoff Institute for Physics, Heidelberg University, 69120 Heidelberg, Germany

[+] Centre for Advanced Materials, Heidelberg University, 69120 Heidelberg, Germany

[⊥] Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS, Université Paris Sud, Université Paris Saclay, 91405 Orsay Cedex, France

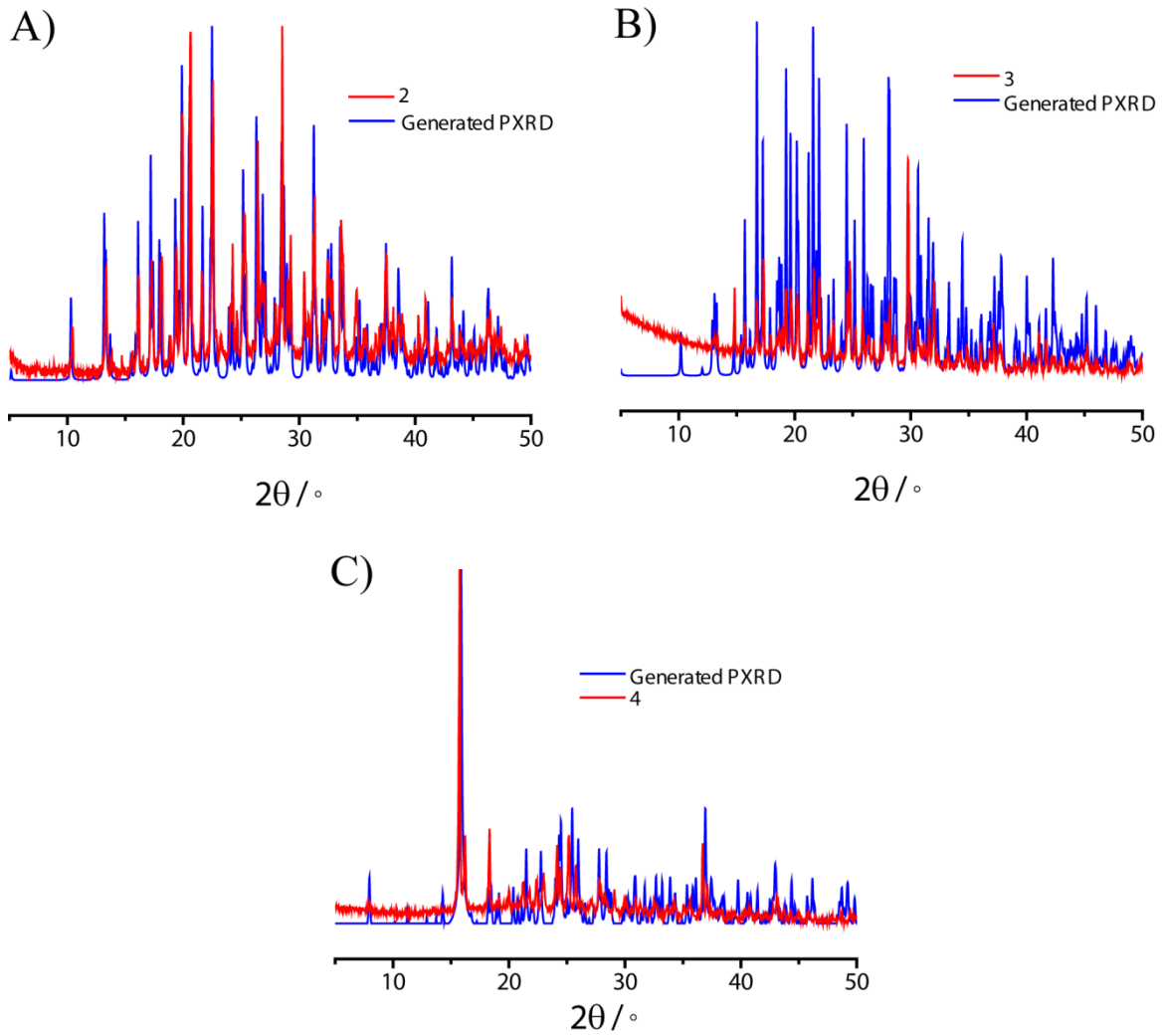

Figure S1. Powder XRD pattern for complexes A) **2**, B) **3** and C) **4**

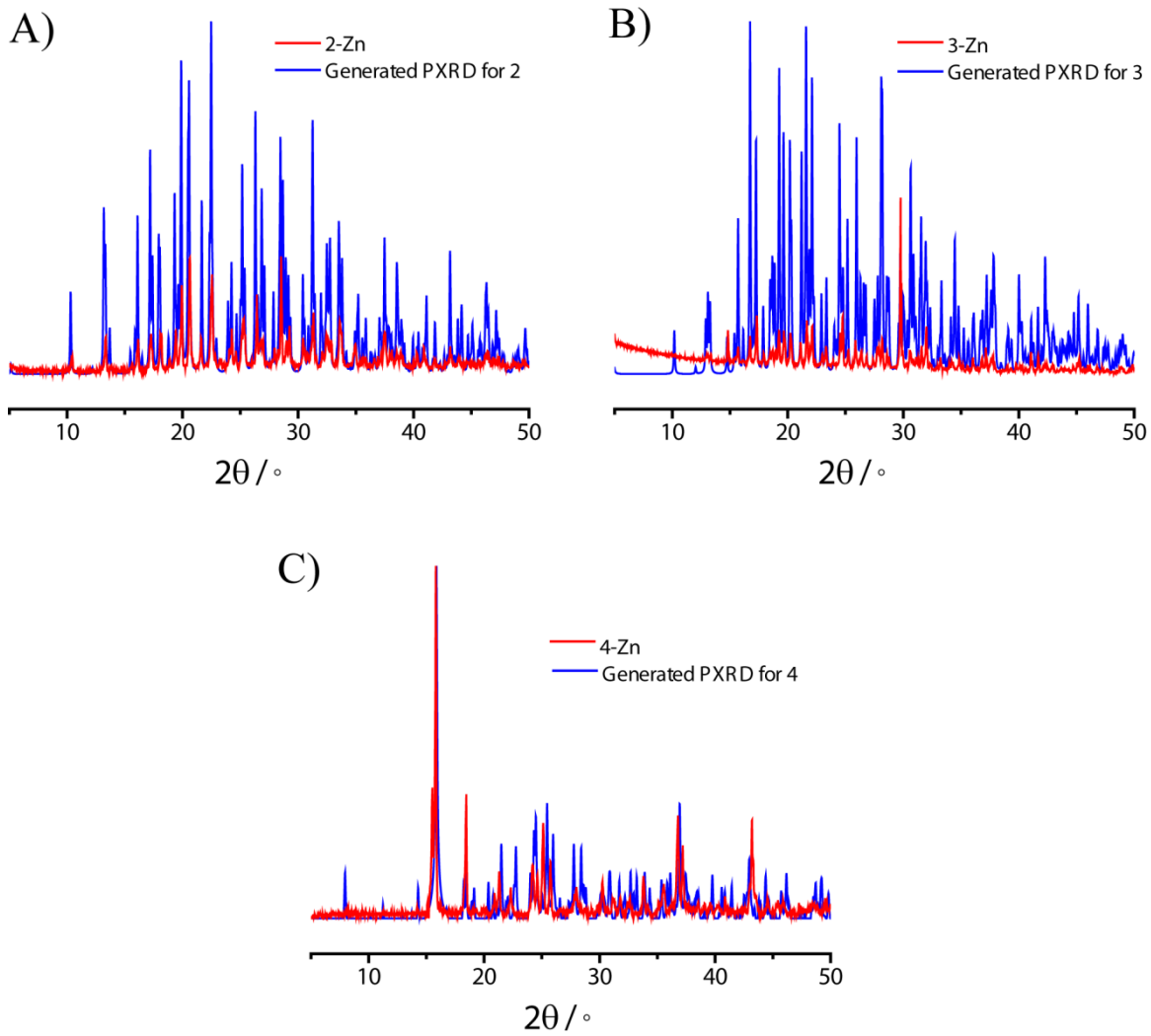

Figure S2. Powder XRD pattern for complexes A) **2-Zn**, B) **3-Zn** and C) **4-Zn**

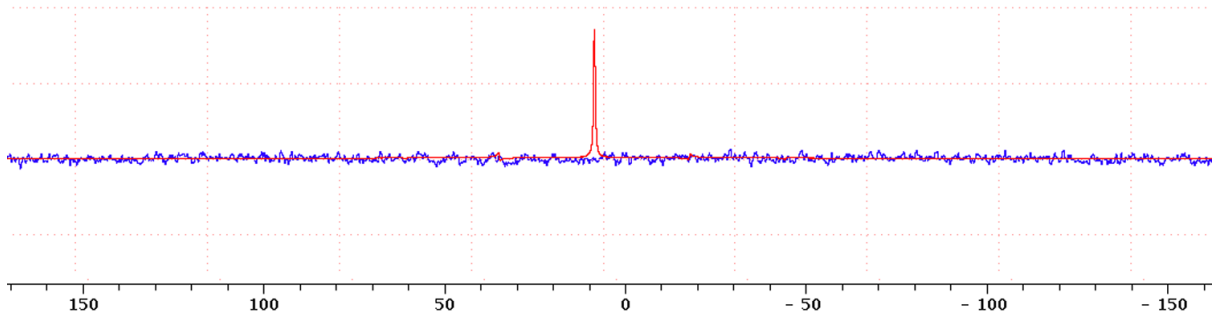

Figure S3. Solid state ^{31}P- magic angle spinning (^{31}P-MAS) NMR recorded with a spinning rate of 10 kHz for 4 (solid blue trace; 128 scans). The solid red trace is for Adenosine Di-Phosphate (ADP) with 2 scans used as a standard.

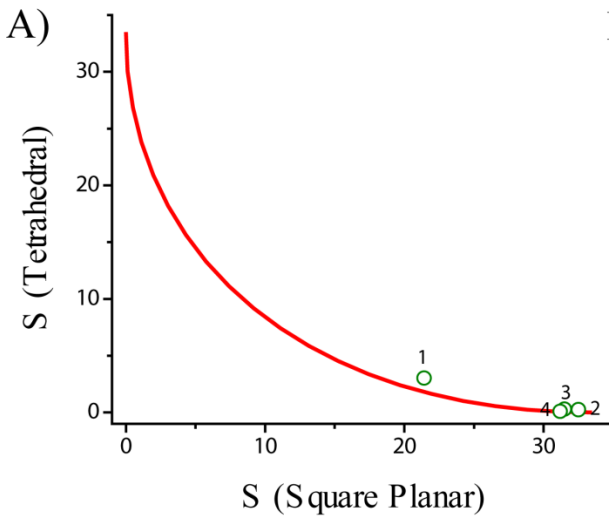

Figure S4. CShM analysis for the co-ordination geometries of the complexes **1-4.**

Table S1. CShM parameters for the co-ordination geometries of the complexes **1-4.**

	1	**2**	**3**	**4**
S (Tetrahedral)	3.01	0.28	0.22	0.09
S (Square planar)	21.42	31.5	32.5	31.2
Φ_Q (T→P)	26.7 %	8.15 %	7.7 %	4.8 %

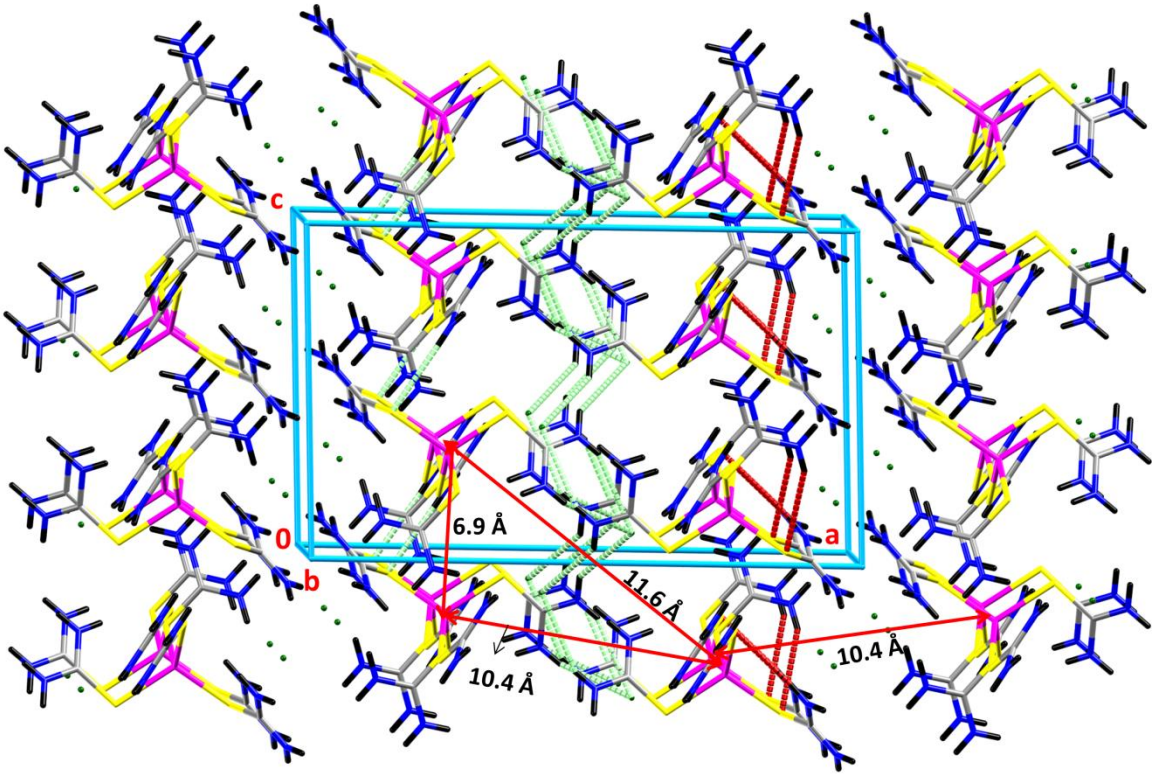

Figure S5. Packing diagram of **3**. Dotted maroon lines represent intramolecular hydrogen bonding and dotted orange lines represent intermolecular hydrogen bonding.

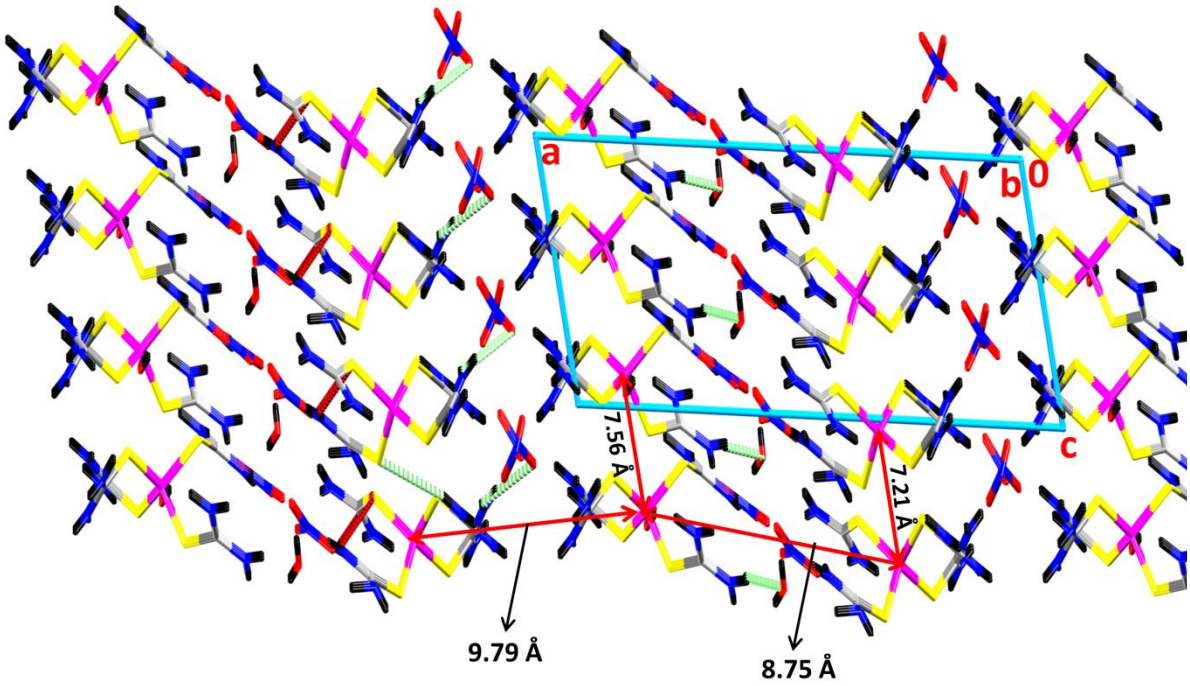

Figure S6. Packing diagram of complex **1**. Dotted maroon lines represent intramolecular hydrogen bonding, whereas green dotted lines represent intermolecular hydrogen bonding. Colour scheme: Pink (Co(II)), Yellow (S), Grey (C), Blue (N), Red (O) and Black (H)

Table S2. Atoms involved in intermolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **2.**

$1 = 1-x,-0.5+y,1.5-z ; $2 = +x,1.5-y,0.5+z ; $3 = 1-x,-0.5+y,0.5-z; $4 = 1-x,2-y,1-z; $5 = -x,-0.5+y,1.5-z; $6 = +x,1+y,+z; $7 = -x,2-y,1-z

H-Bond Donor(D)-Acceptor(A)	D….A (Å)A (Å)	∠DHA (°)
N11-H11A...Br51_$1	3.412(3)	154.4
N12-H12A...Br51_$1	3.417(3)	153.8
N11-H11B...Br61_$2	3.447(4)	152.9
N31-H31B...S21_$2	3.468(4)	176.0
N22-H22B...Br51_$3	3.403(4)	157.3
N21-H21A...Br51_$4	3.505(3)	136.6
N41-H41A...Br61_$5	3.399(4)	154.0
N42-H42A...Br61_$5	3.384(4)	155.1
N31-H31A...S11_$6	3.510(3)	137.1
N42-H42B...Br61_$7	3.376(4)	148.5
N22-H22A...Br51	3.358(3)	175.4
N12-H12B...S21	3.627(4)	154.7
N21-H21B...S31	3.403(4)	166.3
N41-H41B...S11	3.348(4)	160.7
N31-H31A...Br61	3.687(4)	142.4
N32-H32A...Br61	3.309(4)	161.2
N32-H32B...S41	3.287(4)	161.4

Table S3. Atoms involved in intermolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **3.**

H-Bond Donor(D)-Acceptor(A)	D….A (Å)A (Å)	∠DHA (°)
N12-H12A...I61_$1	3.653(3)	152.9
N11-H11B...I61_$2	3.611(3)	140.8
N31-H31B...S41_$2	3.507(3)	175.7
N22-H22A...I51_$3	3.636(2)	156.2
N21-H21A...I51_$3	3.632(3)	156.2
N22-H22B...I61_$4	3.682(3)	155.0
N31-H31A...I61_$5	3.952(3)	142.1
N32-H32A...I61_$5	3.525(3)	160.8
N31-H31A...S21_$6	3.586(3)	138.8
N42-H42A...I51_$7	3.659(2)	141.4
N41-H41B...I51_$8	3.593(3)	155.8
N12-H12B...S21	3.382(3)	160.7
N21-H21B...S41	3.653(3)	152.8
N32-H32B...S11	3.283(3)	166.1
N42-H42B...S31	3.380(3)	169.8
N41-H41A...I51	3.570(3)	164.5

$1 = +x, +y, z+1; $2 = +x, -y+0.5, z+0.5; $3 = -x, y-0.5, -z+1.5; $4 = -x-1, -y, -z+1; $5 = -x-1, y+0.5, -z+0.5; $6 = x, y+1, z; $7 = -x, -y+1, -z+1; $8 = -x, y-0.5, -z+0.5

Table S4. Atoms involved in intermolecular hydrogen bonding and its corresponding bond distance and bond angles in complex **4.**

H-Bond Donor(D)-Acceptor(A)	D….A (Å)A (Å)	∠DHA (°)
N31-H31A...F56_$1	2.840(5)	153.3
N32-H32A...F56_$2	3.067(5)	123.9
N32-H32B...S21_$3	3.565(4)	166.4
N42-H42B...F54_$4	3.193(5)	165.1
N42-H42B...F53_$4	3.039(5)	133.5
N11-H11A...F51_$5	2.853(5)	166.9
N12-H12A...F55_$5	3.199(6)	139.4
N12-H12A...F53_$5	3.002(6)	155.1
N21-H21A...F51_$6	2.801(5)	160.6
N22-H22A...F51_$6	3.234(5)	137.3
N22-H22A...F52_$6	3.364(5)	146.0
N22-H22A...F56_$6	3.245(5)	156.0
N22-H22B...F54_$7	2.964(5)	158.3
N22-H22B...F55_$7	3.052(5)	120.7
N22-H22B...F56_$7	3.254(6)	140.0
N12-H12B...F51_$8	3.342(6)	139.6
N12-H12B...F52_$8	3.014(6)	117.6
N12-H12B...F53_$8	3.039(6)	159.6
N41-H41A...F54	2.816(5)	168.4

N41-H41B...S11	3.618(4)	152.0
N42-H42A...F52	2.818(5)	168.9
N31-H31B...S41	3.407(4)	168.5
N11-H11B...S31	3.323(4)	162.0
N21-H21B...S41	3.596(5)	160.4

$1 = X-1/2, Y, -Z+3/2; $2 = -X+3/2, Y-1/2, Z; $3 = -X+1, -Y, -Z+1; $4 = -X+3/2, Y+1/2, Z; $5 = -X+3/2, -Y, Z-1/2; $6 = -X+3/2, -Y+1, Z-1/2; $7 = X-1/2, -Y+1/2, -Z+1; $8 = X, -Y+1/2, Z-1/2.

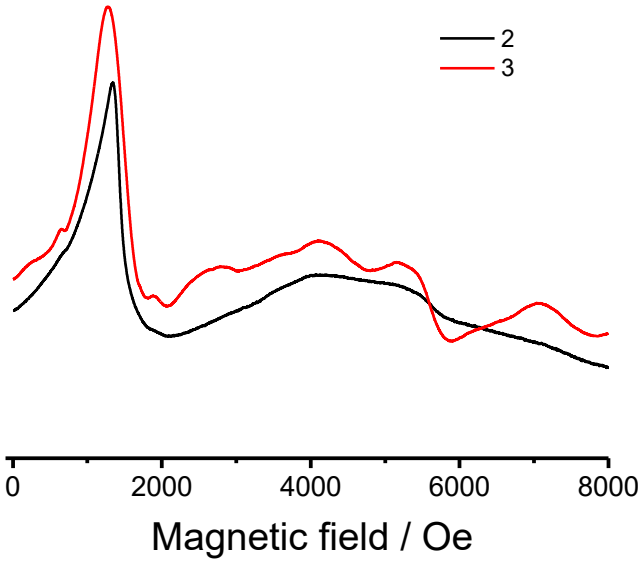

Figure S7. X-band EPR spectrum of complexes **2** and **3** (both 100% samples) performed at 5 K. Experimental conditions: For **2**: Frequency = 9.3744 GHz, Microwave power = 16 dB, modulation amplitude = 0.1 mT; For **3**: Frequency = 9.3725 GHz, Microwave power = 16 dB, modulation amplitude = 0.1 mT.

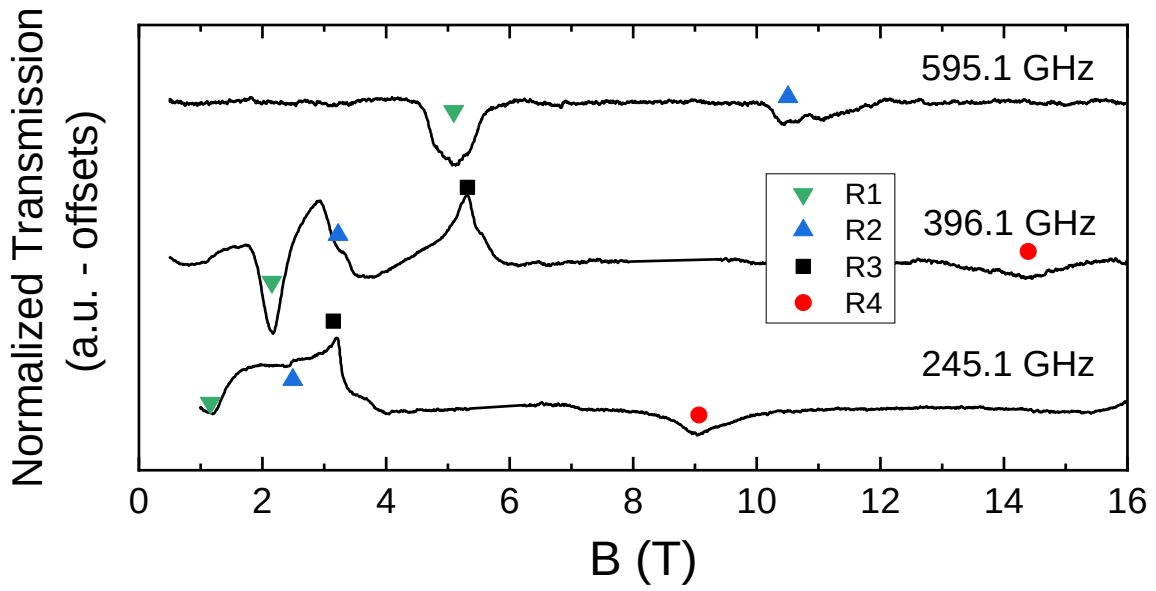

Figure S8: Exemplary HF-EPR transmission spectra measured on complex **3**. Markers label resonance branches as in Fig. 6. The shape of several resonance features (e.g., at f = 245.1GHz, B = 3T) is due to phase mixing effects (see the main manuscript text).

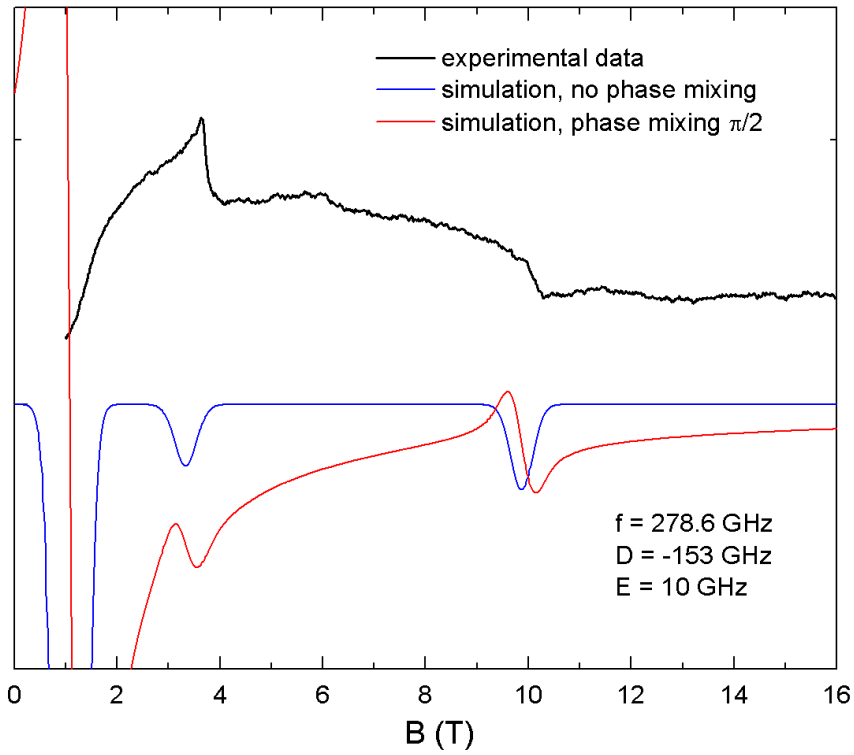

Figure S9: Simulation of experimental HF-EPR for complex **3** with indicated parameters.

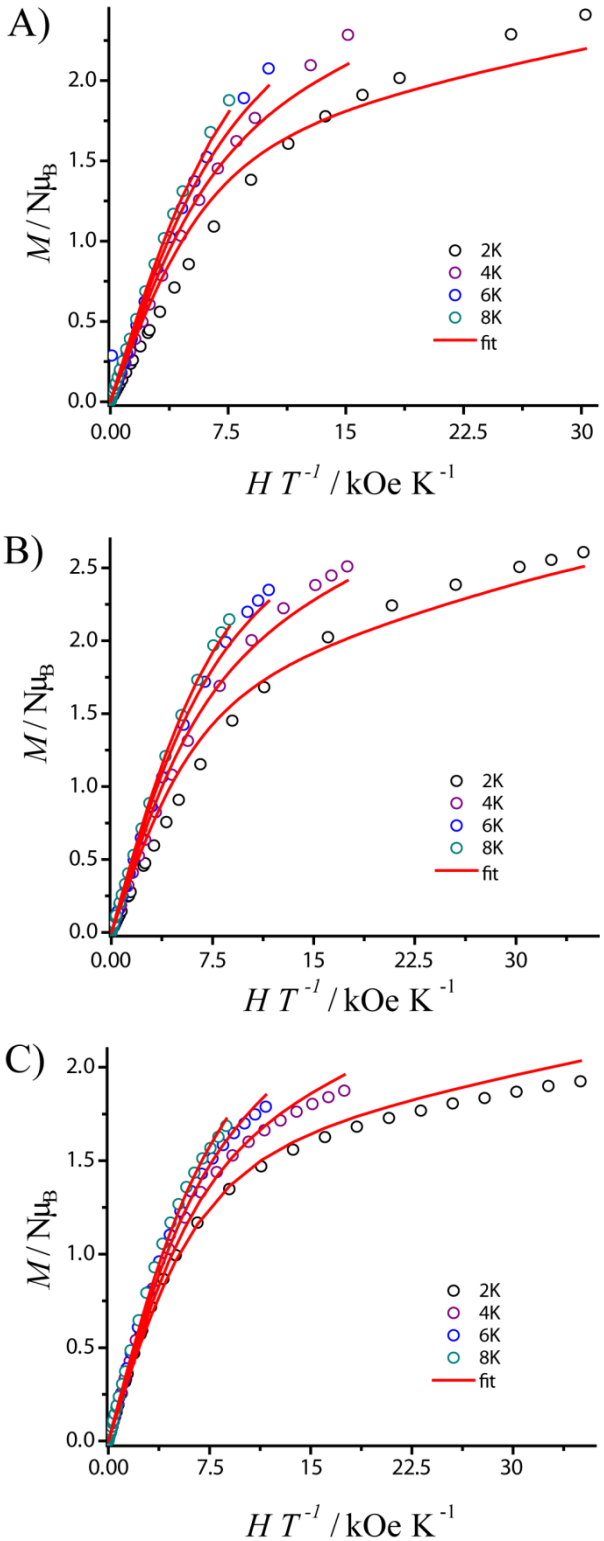

Figure S10. Reduced magnetization of complexes A) **2**, B) **3**, C) **4**. Solid red line represents best fit obtained for the parameters described in table 3 in main script.

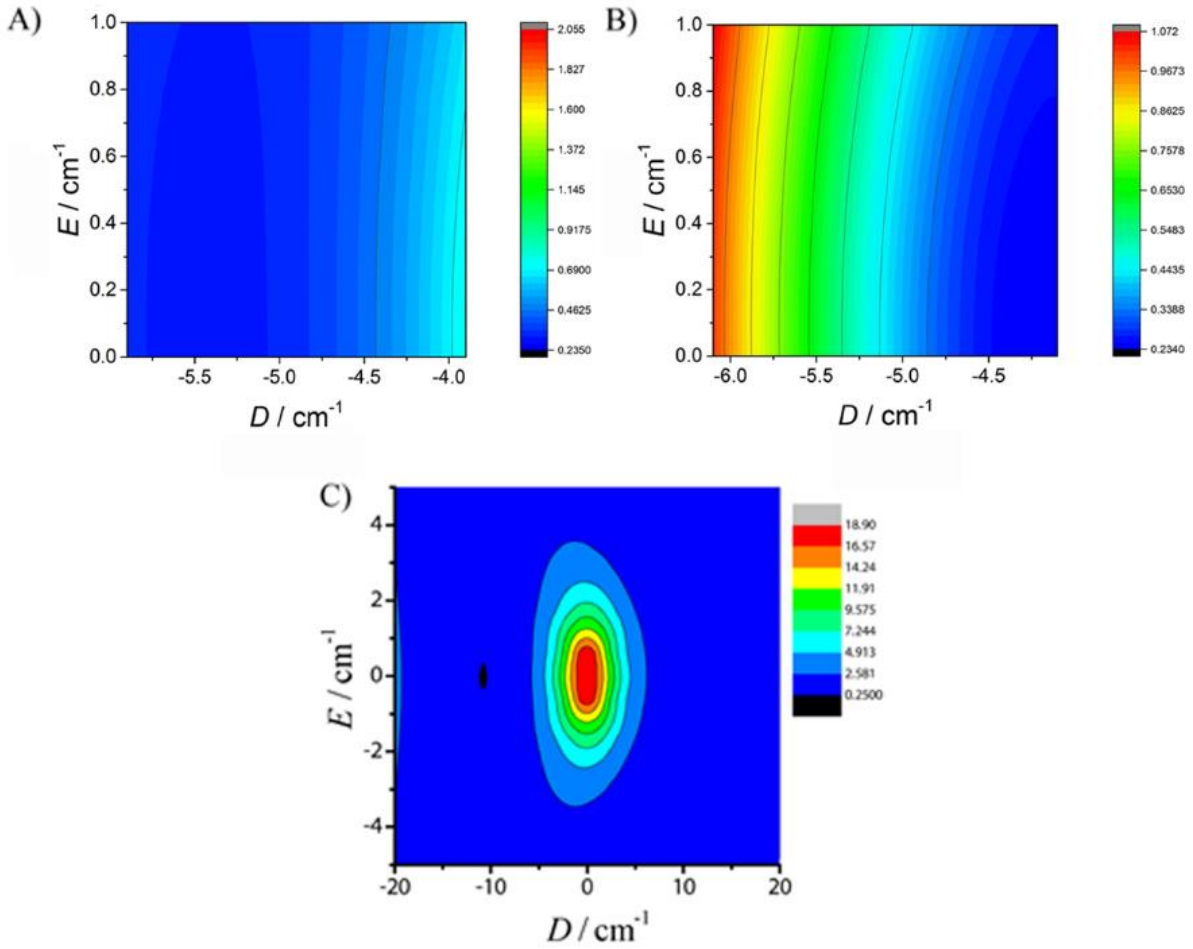

Figure S11. The magnetic data for complexes 2-4 can be fitted using multiple parameters which are shown by the error plots for complexes A) **2**, B) **3** and C) **4**.

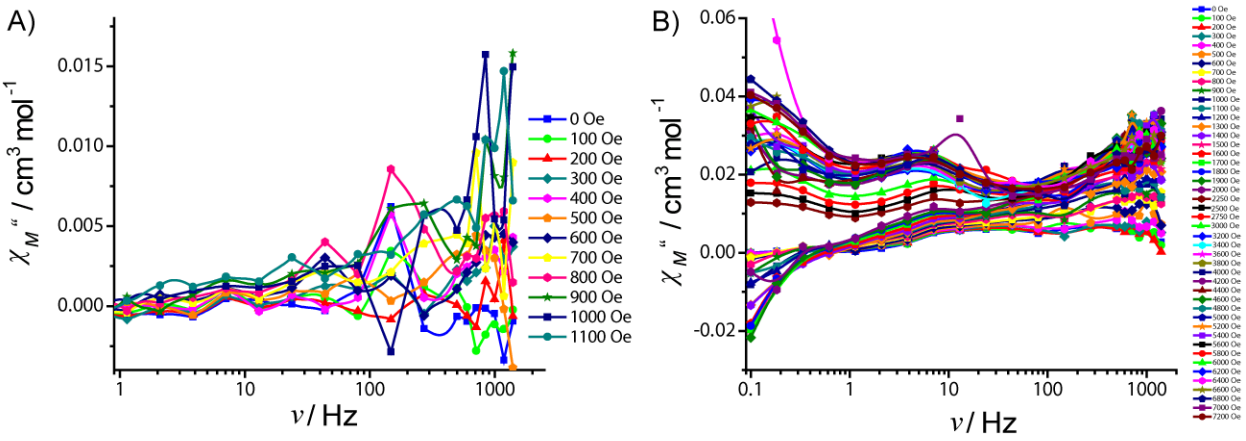

Figure S12- Field sweep out-of-phase susceptibility data of **2** (panel A) and **4** (Panel B).

Table S5: CASSCF(7,5) computed Spin-Hamiltonian parameter (g, *D*, |E/D|) along with listed state-by-state contribution to the *D* and E values. The SH parameters extracted from the calculations in the presence of anions are given in parenthesis.

States	**1a**	**1a**	**1a**	**1b**	**1b**	**1b**	States	**2**	**2**	**2**	**3**	**3**	**3**	States	**4**	**4**	**4**
		CASSCF			CASSCF				CASSCF			CASSCF				CASSCF	
	Energy (cm^{-1})	Contribution to *D* (cm^{-1})	Contribution to *E* (cm^{-1})	Energy (cm^{-1})	Contribution to *D* (cm^{-1})	Contribution to *E* (cm^{-1})		Energy (cm^{-1})	Contribution to *D* (cm^{-1})	Contribution to *E* (cm^{-1})	Energy (cm^{-1})	Contribution to *D* (cm^{-1})	Contribution to *E* (cm^{-1})		Energy (cm^{-1})	Contribution to *D* (cm^{-1})	Contribution to *E* (cm^{-1})
$^4T_2$(F)	880.6(851.6)	-98.68(-102.49)	-0.02(-0.08)	1042.60(1037.1)	-89.99(-89.99)	-0.02(0.002)	$^4A_1$(F)	2880.5(2864.9)	-29.86(29.81)	-1.89(-3.34)	2869(2888.8)	-32.92(-32.02)	0.12(2.25)	$^4A_1$ (F)	2867.7(2782.4)	-38.18/(17.62)	0.32/(19.10)
	3677.0(3672.5)	14.08(13.67)	-14.27(-14.51)	4035.82(3859.2)	12.22(10.32)	-12.34(-10.33)	4E(F)	3181.8(3242.2)	7.67(10.53)	4.21(7.54)	3219(3200.5)	16.76(14.75)	-5.85(-6.71)	$^4B_1$ (F)	3125.8(3149.2)	14.44/(12.76)	-13.17/(-15.52)
	4656.0(4683.7)	2.06(1.29)	1.63(1.28)	4673.47(4452.5)	6.89(7.96)	5.91(4.82)			14.54(8.50)	-3.19/(-6.16)	5314(3286.7)	9.34(11.06)	4.33(3.40)	$^4B_2$ (F)	3992.0(3999.4)	12.54/(-18.55)	10.14/(-0.09)
D_{tol}		-69.07(-74.08)			-60.53(-61.04)				-7.64(-10.36)			-6.92(-4.38)				-10.45/(±10.63)	
|E/D|		0.04(0.03)			0.03(0.03)				0.09(0.18)			0.16(0.17)				0.19/(0.33)	
g_x		2.12(2.08)			2.15(2.15)				2.23(2.29)			2.32(2.21)				2.27/(2.26)	
g_y		2.22(2.15)			2.21(2.21)				2.22(2.33)			2.34(2.23)				2.33/(2.34)	
g_z		2.97(2.7)			2.89(2.89)				2.27(2.43)			2.41(2.27)				2.47/(2.42)	

Table S6- The basis sets describing all atoms were taken from ANO-RCC library available in MOLCAS 8.0 package.

Elements	Basis Set
Zn	ANO-RCC...6s5p3d2f1g
Co	ANO-RCC...5s4p2d
C	ANO-RCC...4s3p2d
N	ANO-RCC...2s1p
O	N.ANO-RCC...5s4p2d
H	ANO-RCC...3s2p1d
S	ANO-RCC...2s1p and ANO-RCC...5s4p2d1f

Table S7. The *ab intio* computed *SH* parameters for complexes **1-4** obtained using MOLCAS set up ([a] = without/ [b] = with anion).

	1a	**1b**	**2**	**3**	**4**
D (cm^{-1})	−62.8 [a] /-71.15 [b]	−51.9 [a] /-62.16 [b]	-7.55 [a] /-9.63 [b]	-6.76 [a] /-8.86 [b]	-10.05 [a] /±7.52 [b]
|E/D|	0.05 [a] /0.047 [b]	0.05 [a] /0.02 [b]	0.14 [a] /0.25 [b]	0.18 [a] /0.25 [b]	0.22 [a] /0.28 [b]
g_{xx}	2.16 [a] /2.12 [b]	2.18 [a] /2.16 [b]	2.32 [a] /2.42 [b]	2.32 [a] /2.30 [b]	2.28 [a] /2.40 [b]
g_{yy}	2.26 [a] /2.23 [b]	2.27 [a] /2.21 [b]	2.35 [a] /2.37 [b]	2.35 [a] /2.35 [b]	2.34 [a] /2.36 [b]
g_{zz}	2.93 [a] /2.98 [b]	2.84 [a] /2.88 [b]	2.42 [a] /2.29 [b]	2.41 [a] /2.42 [b]	2.42 [a] /2.29 [b]

Table S8. Spin orbital coupling constant obtained for complexes **1**-**4**.

Complex	Spin Orbit Coupling Constant (ζ)/ cm^{-1}
1a	503.4
1b	502.4
2	502.5
3	503.0
4	512.8