Supplementary information

Field-induced Single Ion Magnet behaviour in discrete and one-dimensional complexes containing the bis(1-methylimidazol-2-yl)ketone]-containing cobalt(II) building units

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I. FTIR spectra

The infrared spectra of **1**-**2** are similar and all of them show typical peaks of the ^{Me}bik ligand in the fingerprint region. A characteristic C=O stretching vibration is also observed at 1640 and 1638 cm^{-1} in **1**-**2**, respectively. The bound *N*-thiocyanate (**1**) and *N*-selenocyanate (**2**) show intense absorptions at 2100 and 2066 cm^{-1} (**1**) and 2097 and 2069 cm^{-1} (**2**). These peaks are associated with the stretching modes ν(CN) in the two coligands. The infrared spectrum for **3** shows two peaks at 2185 and 2142 cm^{-1}, which are assigned to the stretching vibrations of the bridging and terminal cyanide groups, respectively. As expected, these absorption peaks occur at higher frequencies compared to that of the free dicobalt(III) metalloligand (*ca*. 2130 cm^{-1})[1] but close to those of the related chain $[Co^{II}(CH_3OH)_2(dmso)_2(\mu\text{-}NC)_2Co_2^{III}(\mu\text{-}2,5\text{-}dpp)(CN)_6]_n\cdot 4nCH_3OH$ (ca. 2171 and 2140 cm^{-1}).[2] A strong and broad absorption centred at 3490 cm^{-1} [υ(O-H)] is indicative of the existence of water molecules associated by hydrogen bonds. A multiplet of peaks in the frequency range 3100-2820w cm^{-1} [aromatic and aliphatic υ(C-H)] plus absorptions at 1370s cm^{-1} [υ(C-H) of methyl groups], 1630s, 1486w and 1467m [υ(C=O)]. 1513w, 1441m, 1418vs, 1292w, and 1195s cm^{-1} [υ(C=N) and υ(C=C) stretchings] are a diagnostic of the presence of the 2,5-dpp and ^{Me}bik ligands in 4. The strong absorption at 900 cm^{-1} could be attributed to the υ(S=O) stretching vibration of the coordinated dmso molecule. Finally, the medium intensity peak at 425 cm^{-1} is most likely due to the Co^{II}-O bonds. All these spectroscopic features are confirmed by the X-ray structures (see below).

References:

1. M.-G. Alexandru, N. Marino, D. Visinescu, G. D. Munno, M. Andruh, A. Bentama, F. Lloret and M. Julve, *New J. Chem.*, 2019, **43**, 6675–6682.
2. M.-G. Alexandru, D. Visinescu, S. Shova, A. Bentama, F. Lloret, J. Cano and M. Julve, *Magnetochemistry*, 2020, **6**, 66.

II. X-ray diffraction on single crystals and in powder

Table S1. Bond lengths (Å) and angles (deg) of the cobalt(II) and cobalt(III) coordination environments for **3**.

3					
Co1-N1	1.952(14)	C15-Co1-Co17	88.0(9)	Co3-N9-C19	147.5(15)
Co1-N2	1.972(13)	Co15-Co1-C18	91.9(8)	N9-Co3-N13	91.2(6)
Co1-C15	1.88(2)	Co16-Co1-C17	91.3(10)	N9-Co3-N14	174.8(6)
Co1-C16	1.87(2)	C16-Co1-C18	87.2(8)	N9-Co3-N6a*	92.3(6)
Co1-C17	1.84(2)	C17-Co1-C18	91.2(8)	N9-Co3-O1A	88.9(5)
Co1-C18	1.87(2)	Co1-C15-N5	173.3(16)	N9-Co3-O2	95.1(6)
Co2-N3	1.984(14)	Co1-C16-N6	175.2(17)	Co3-N6a-C16a*	155.5(18)
Co2-N4	1.999(14)	Co1-C17-N7	176(2)	N6a-Co3-N13*	90.3(6)
Co2-C19	1.90(2)	Co1-C18-N8	177(2)	N6a-Co3-N14*	90.4(6)
Co2-C20	1.97(2)	N3-Co2-N4	81.7(6)	N6a-Co3-O1A*	178.5(6)
Co2-C21	1.918(19)	C19-Co2-N3	85.0(6)	N6a-Co3-O2*	94.4(6)
Co2-C22	1.88(2)	C20-Co2-N3	92.2(7)	N13-Co3-O1A	88.8(5)
Co3-N6a*	2.137(17)	C21-Co2-N3	96.1(7)	N13-Co3-O2	172.0(6)
Co3-N9	2.143(18)	C22-Co2-N3	178.1(8)	N14-Co3-O1A	88.3(5)
Co3-N13	2.119(15)	C19-Co2-N4	88.4(7)	N14-Co3-O2	89.1(6)
Co3-N14	2.100(16)	C20-Co2-N4	89.6(7)	O1A-Co3-O2	86.4(5)
Co3-O1A	2.149(11)	C21-Co2-N4	177.0(7)		
Co3-O2	2.074(13)	C22-Co2-N4	97.4(7)		
		C19-Co2-C20	176.8(8)		
N1-Co1-N2	83.7(6)	C19-Co2-C21	93.5(8)		
C15-Co1-N1	89.8(7)	C19-Co2-C22	93.3(8)		
C16-Co1-N1	91.2(7)	C20-Co2-C21	88.4(8)		
C17-Co1-N1	92.6(7)	C20-Co2-C22	89.4(9)		
C18-Co1-N1	175.9(7)	C21-Co2-C22	84.8(7)		
C15-Co1-N2	91.8(7)	Co2-C19-N9	172.2(16)		
C16-Co1-N2	88.9(7)	Co2-C20-N10	178(2)		
C17-Co1-N2	176.3(7)	Co2-C21-N11	178.2(17)		
C18-Co1-N2	92.5(7)	Co2-C22-N12	175(2)		
C15-Co1-C16	178.8(8)	N13-Co3-N14	84.3(6)		

*symmetry code a = *x*, 1-*y*, 1/2+*z*.

Table S2. Geometrical parameters associated to the hydrogen bonds in **X**[a,b]

D---H···A	D – H/ Å	H···A/ Å	D···A/ Å	D - H···A, deg
OA ··· N11m	0.91	1.96	2.799(19)	153
O4W ··· O1W	0.85	1.98	2.71(9)	143
O4W ··· N7n	0.85	2.31	2.97(4)	134
O4W ··· N10m	-	-	2.78	-

[a]D = donor and A = acceptor. [b]Symmetry code: (m) = *x*, -1+*y*, *z*; (n) = -1+*x*, *y*, *z*.

Bond-valence model[a,b] was performed using Platon for **3**.[c] The bond-valence sum for Co atoms are:

Co1 (III) V_{sum} = 3.26, D_{max} = 1.9730, N_{sum} = 6

Co2 (III) V_{sum} = 2.90, D_{max} = 1.9990, N_{sum} = 6

Co3 (II) V_{sum} = 1.99, D_{max} = 2.1480, N_{sum} = 6

Table S3a. Bond Valence Analysis assuming valence = 3 for **3**.

Nr	Bond	Distance	R	B	Bval	Sum	Diff
1	Co1 - C17	1.8400	1.6340	0.37	0.573	0.573	2.427
2	Co1 - C16	1.8690	1.6340	0.37	0.530	1.103	1.897
3	Co1 - C18	1.8740	1.6340	0.37	0.523	1.626	1.374
4	Co1 - C15	1.8840	1.6340	0.37	0.509	2.134	0.866
5	Co1 - N1	1.9520	1.7500	0.37	0.579	2.714	0.286
6	Co1 - N2	1.9730	1.7500	0.37	0.547	**3.261**	0.261

Table S3b. Bond Valence Analysis assuming valence = 3 for **3**.

Nr	Bond	Distance	R	B	Bval	Sum	Diff
1	Co2 – C22	1.8800	1.6340	0.37	0.514	0.514	2.486
2	Co2 – C19	1.9050	1.6340	0.37	0.481	0.995	2.005
3	Co2 – C21	1.9210	1.6340	0.37	0.460	1.455	1.545
4	Co2 – C20	1.9700	1.6340	0.37	0.403	1.859	1.141
5	Co2 – N3	1.9850	1.7500	0.37	0.530	2.389	0.611
6	Co2 – N4	1.9990	1.7500	0.37	0.510	**2.899**	0.101

Table S3c. Bond Valence Analysis assuming valence = 2 for **3**.

Nr	Bond	Distance	R	B	Bval	Sum	Diff
1	Co3 – O2	2.0740	1.6340	0.37	0.307	0.307	2.693
2	Co3 – N14	2.0990	1.7500	0.37	0.389	0.696	2.304
3	Co3 – N13	2.1180	1.7500	0.37	0.370	1.066	1.934
4	Co3 – N6b	2.1370	1.7500	0.37	0.351	1.418	1.582
5	Co3 – N9	2.1430	1.7500	0.37	0.346	1.763	1.237
6	Co3 – OA	2.1480	1.6370	0.37	0.251	**2.015**	0.985

a. N. E. Brese, M. O'Keeffe, Acta Cryst. B 1991, 47, 192.

b. I. D. Brown, The Chemical Bond in Inorganic Chemistry: The Bond Valence Model. 2002, Oxford University Press.

c. A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1998.

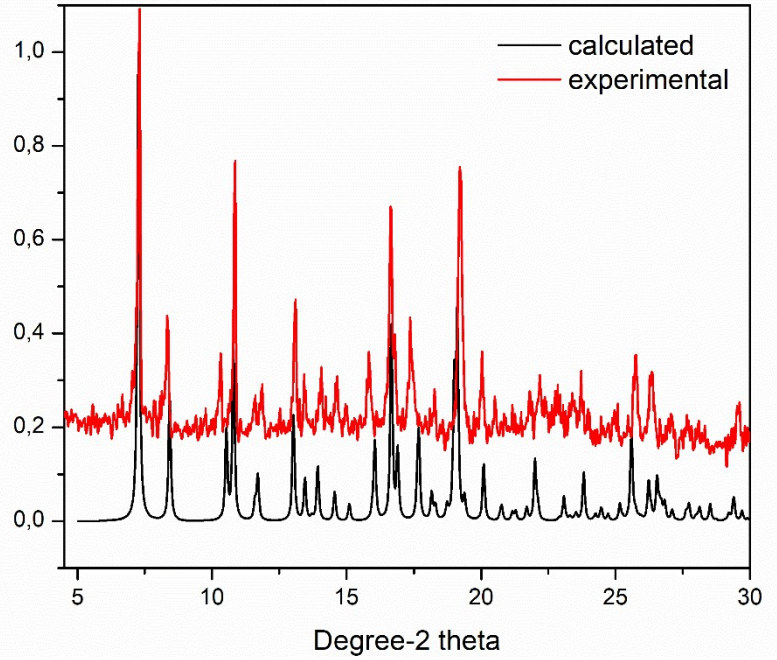

Fig. S1. Calculated and experimental X-ray diffraction patterns for compound **3**.

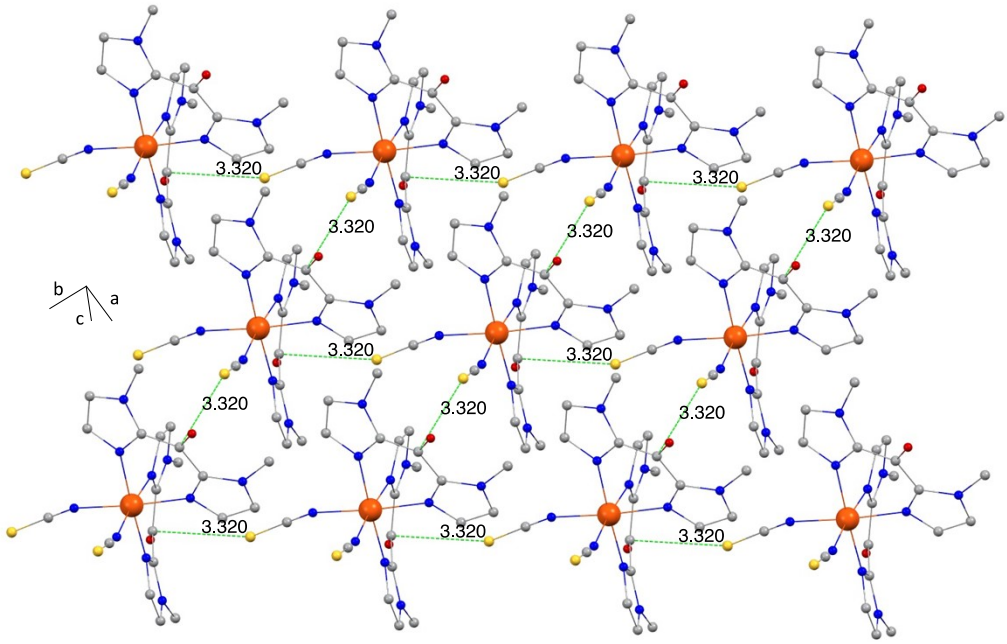

Fig S2a. Supramolecular layer of **1** formed by S-C short contacts. H atoms were omitted for the sake of clarity.

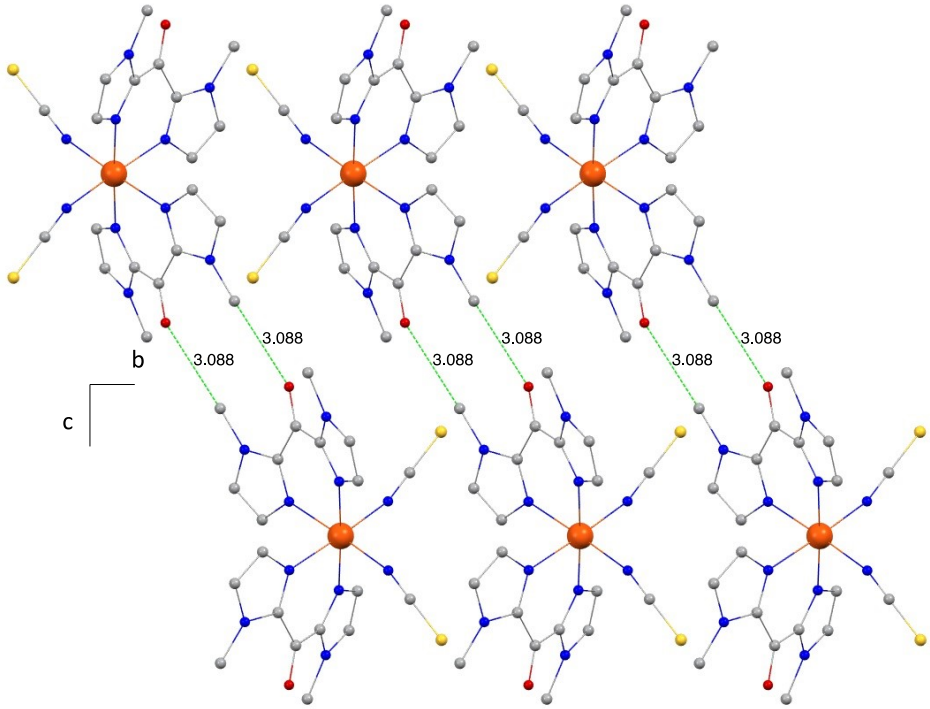

Fig S2b. C-O interlayer contacts of **1**, view from a direction. H atoms were omitted for the sake of clarity.

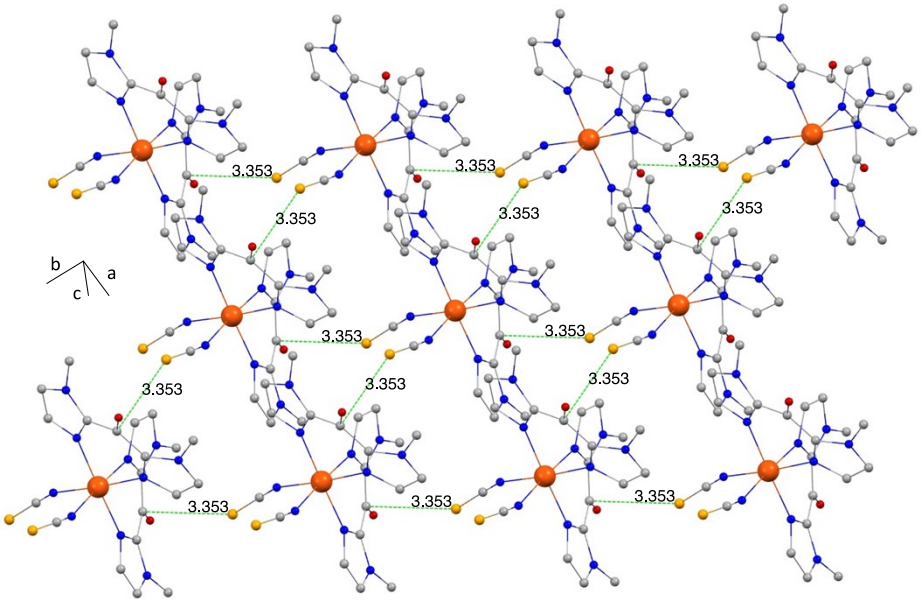

Fig S3a. Supramolecular layer of **2** formed by Se-C short contacts. H atoms were omitted for the sake of clarity.

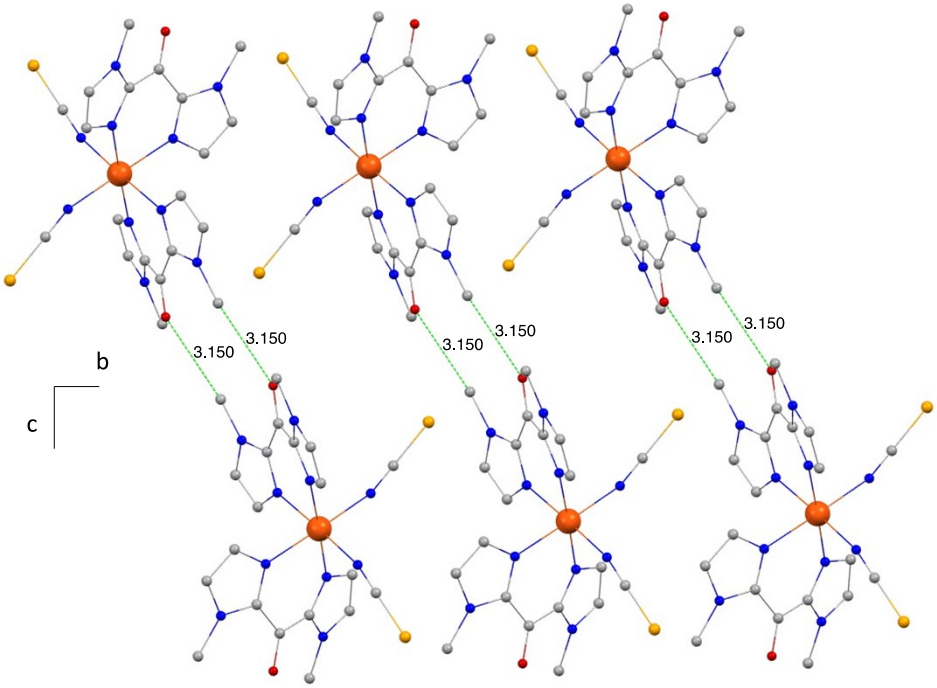

Fig S3b. C-O interlayer contacts of **2**. H atoms were omitted for the sake of clarity.

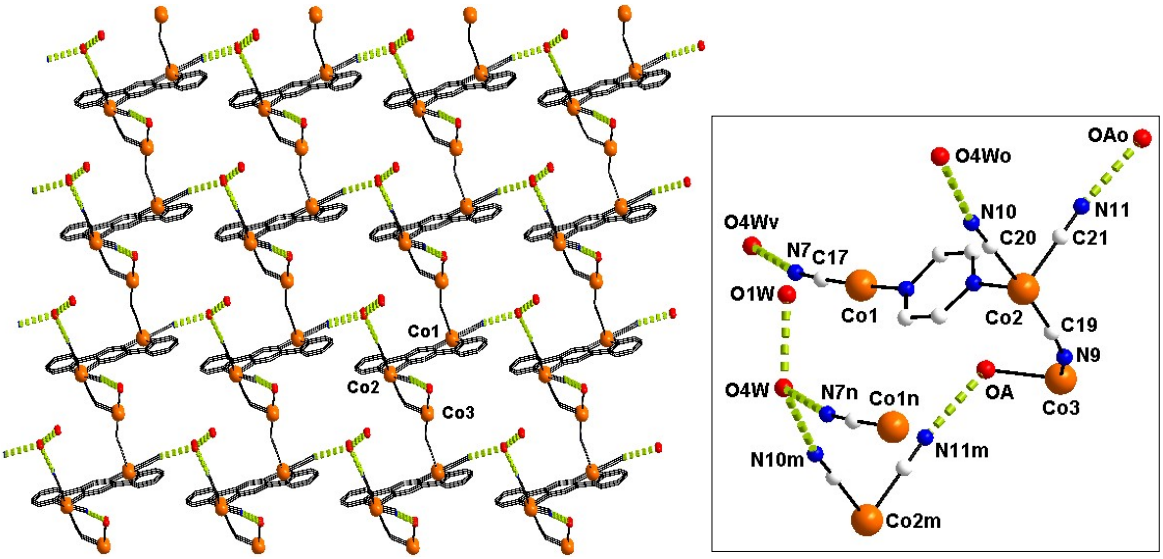

Fig S4. (Left) View of a fragment of the supramolecular 3D structure through hydrogen bonds. (Right) A detailed view of the hydrogen bond pattern [symmetry code: (m) = *x*, -1+*y*, *z*; (n) = -1+*x*, *y*, *z*; (o) = *x*, 1+*y*, *z*].

III. Ab-initio calculations

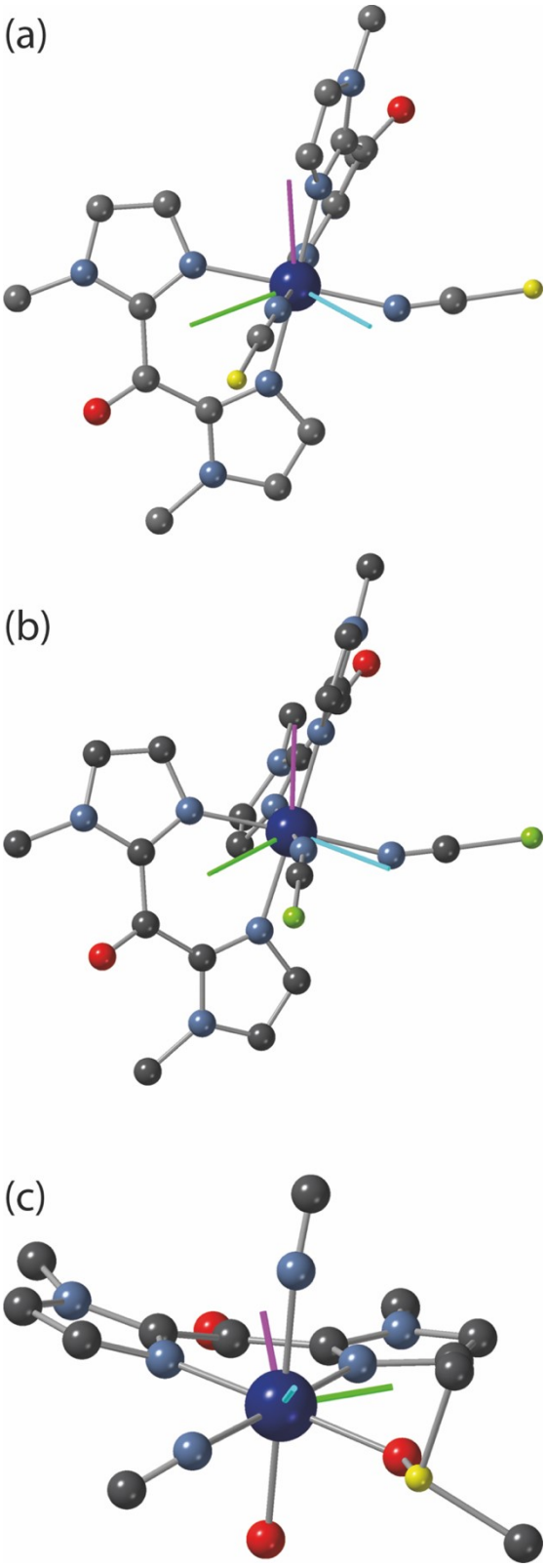

Figure S5. Relative orientation of the experimental coordination sphere geometry of **1-3** (a-c) and the calculated *D* tensor (*x* = cyan, *y* = green, *z* = magenta). Colour code: green, cobalt; blue, nitrogen; red, oxygen; grey, carbon; yellow, sulphur.

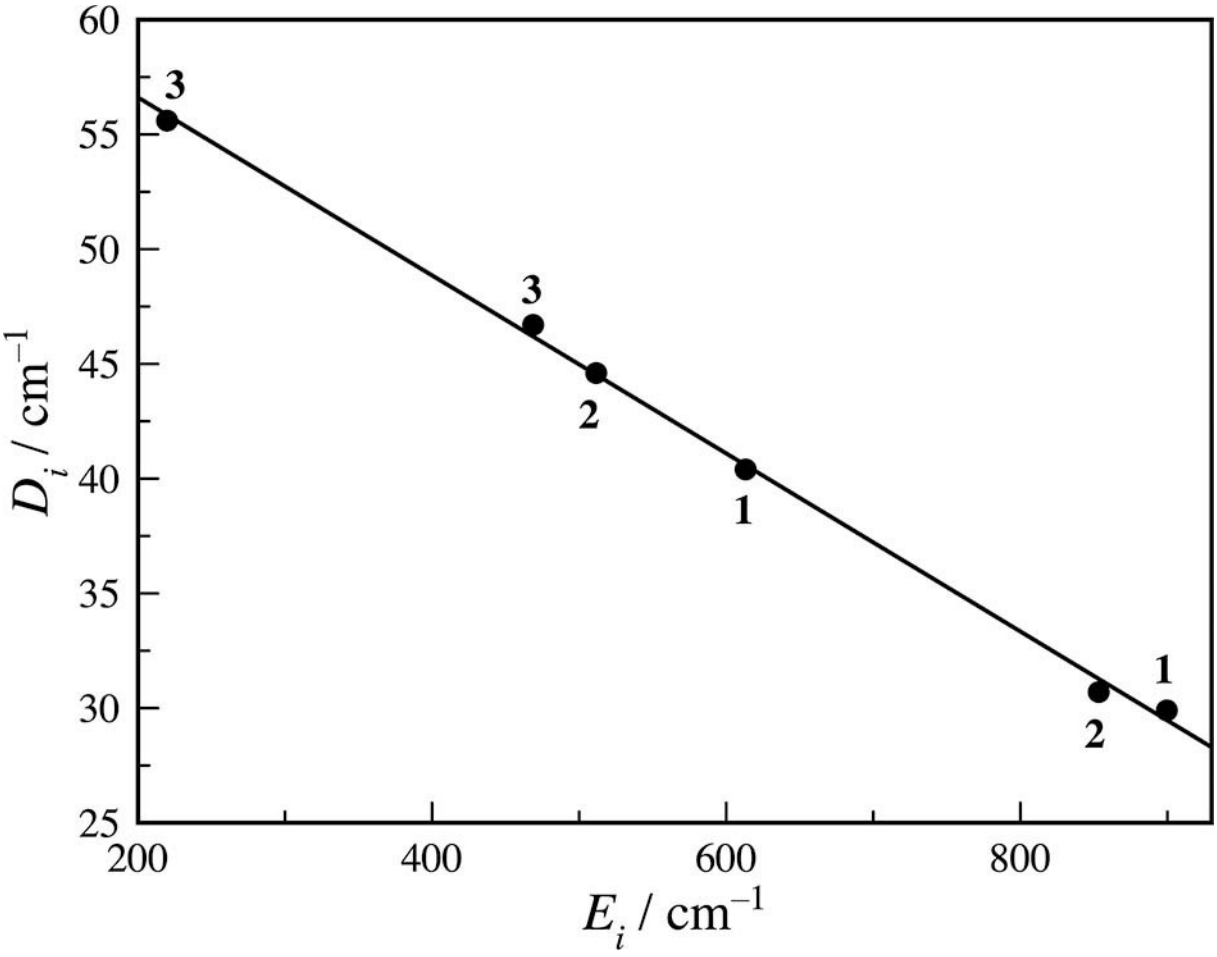

Figure S6. Energy dependence of the D_i contributions for the two first quartet excited states for **1**-**3**. Labels are provided to identify the data for each compound.

IV. EPR spectra and magnetic measurements in AC mode

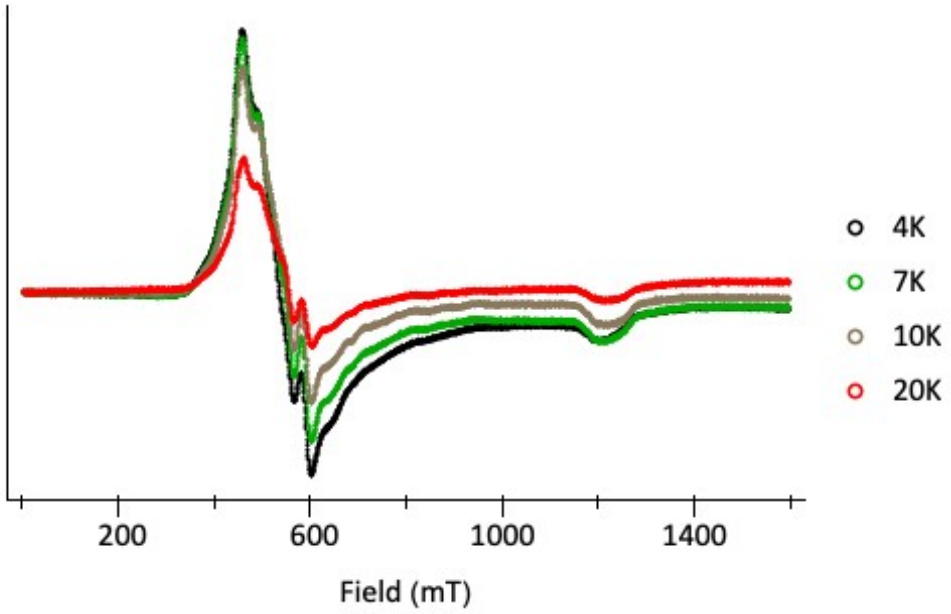

Figure S7. Q band powder EPR spectra of 4 at different temperatures from 4 K to 20 K.

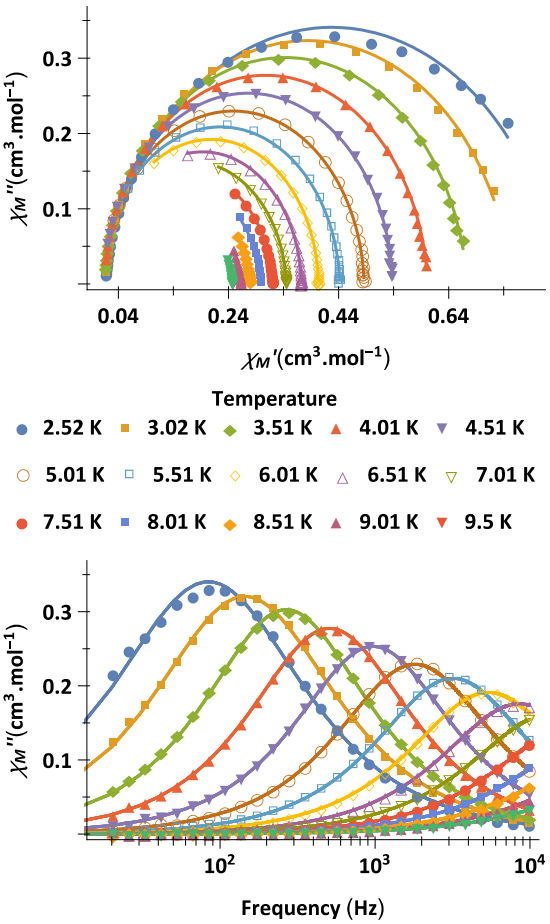

Fig S8. CCP and χ''_M versus Frequency (logarithmic scale) for **1** at temperature of 2.5- 9.5 K. the solid lines are the fits of the data to a generalized Debye model.

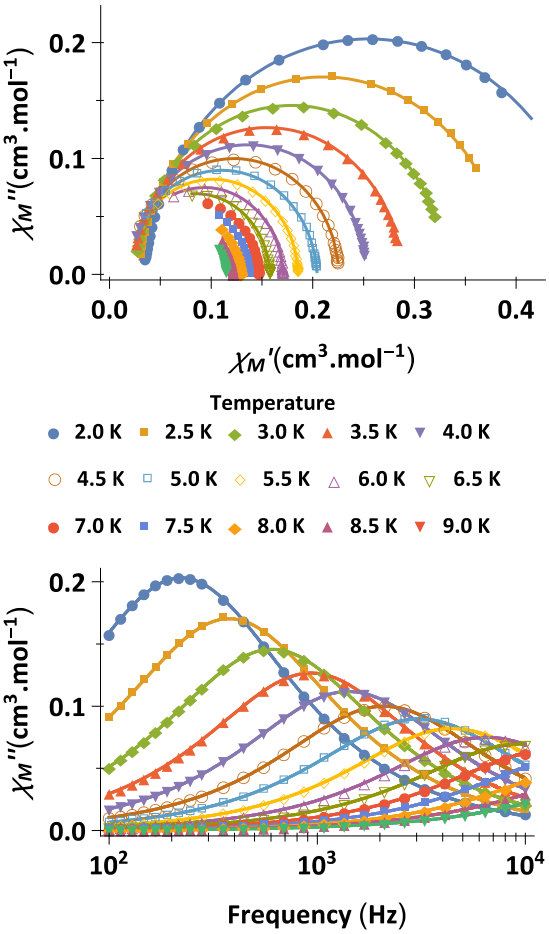

Fig S9. CCP and χ''_M versus Frequency (logarithmic scale) for **4** at temperature of 2.0- 9.0 K. the solid lines are the fits of the data to a generalized Debye model.

Table S4. The best fitted parameters of Cole-Cole Plot, χ'_M versus Log F and χ'_M versus Log F for **1** under an applied field of 0.16 T

T (K)	X_S (cm^3mol^{-1})	X_T (cm^3mol^{-1})	α	τ(s)
2.520	0.013	0.855	0.134	0.0019133
3.015	0.012	0.770	0.106	0.0011161
3.512	0.014	0.669	0.050	0.0005941
4.009	0.013	0.602	0.038	0.0003131
4.510	0.013	0.538	0.023	0.0001637
5.009	0.011	0.486	0.023	0.0000878
5.508	0.013	0.443	0.014	0.0000502
6.006	0.007	0.406	0.027	0.0000295
6.507	0.008	0.373	0.024	0.0000186
7.006	0.004	0.345	0.033	0.0000118
7.505	0.001	0.321	0.041	0.0000078
8.004	0.000	0.300	0.057	0.0000053
8.504	0.000	0.280	0.069	0.0000036
9.004	0.000	0.263	0.082	0.0000025
9.504	0.000	0.248	0.098	0.0000018

Table S5. The best fitted parameters of Cole-Cole Plot, χ'_M versus Log F and χ'_M versus Log F for **2** under an applied field of 0.17 T

T (K)	X_S (cm^3mol^{-1})	X_T (cm^3mol^{-1})	α	τ(s)
2.498	0.019	0.493	0.051	0.0018176
2.751	0.018	0.463	0.048	0.0014267
3.001	0.018	0.436	0.046	0.0011072
3.251	0.017	0.409	0.042	0.0008368
3.501	0.016	0.384	0.036	0.0006171
3.750	0.016	0.362	0.030	0.0004494
4.000	0.016	0.340	0.022	0.0003244
4.251	0.015	0.322	0.019	0.0002343
4.500	0.015	0.306	0.017	0.0001702
4.750	0.015	0.289	0.008	0.0001246
5.000	0.015	0.277	0.009	0.0000927
5.250	0.015	0.264	0.007	0.0000694
5.499	0.014	0.252	0.007	0.0000529
5.749	0.013	0.243	0.012	0.0000406
5.999	0.014	0.233	0.008	0.0000318
6.249	0.014	0.224	0.011	0.0000250
6.499	0.010	0.217	0.024	0.0000195
6.749	0.016	0.208	0.008	0.0000162
6.999	0.011	0.202	0.022	0.0000128
7.248	0.010	0.195	0.026	0.0000103
7.498	0.003	0.189	0.036	0.0000082
7.748	0.000	0.183	0.047	0.0000066
7.998	0.000	0.178	0.055	0.0000054

Table S6. The best fitted parameters of Cole-Cole Plot, χ'_M versus Log F and χ'_M versus Log F for **3** under an applied field of 0.25 T

T (K)	X_S (cm^3mol^{-1})	X_T (cm^3mol^{-1})	α	τ(s)
2.011	0.026	0.538	0.079	0.001147858
2.255	0.023	0.537	0.101	0.001019411
2.505	0.022	0.500	0.089	0.000823262
2.752	0.020	0.486	0.099	0.000700725
3.003	0.018	0.464	0.104	0.000583578
3.250	0.016	0.450	0.119	0.000499556
3.497	0.015	0.420	0.116	0.000402851
3.748	0.013	0.407	0.133	0.000344006
3.995	0.013	0.377	0.122	0.000274130
4.243	0.011	0.366	0.137	0.000234561
4.496	0.009	0.356	0.154	0.000199635
4.741	0.009	0.338	0.152	0.000164586
4.991	0.010	0.316	0.135	0.000131007
5.241	0.012	0.296	0.109	0.000105071
5.488	0.009	0.289	0.129	0.000088648
5.738	0.011	0.276	0.113	0.000072623
5.986	0.013	0.266	0.103	0.000060729
6.235	0.018	0.252	0.072	0.000050286
6.476	0.020	0.241	0.061	0.000041740
6.728	0.021	0.235	0.062	0.000035395
6.983	0.019	0.228	0.072	0.000029159
7.231	0.017	0.222	0.085	0.000023868
7.479	0.027	0.212	0.046	0.000021044
7.729	0.026	0.207	0.053	0.000017441
7.976	0.040	0.198	0.053	0.000016201
8.226	0.026	0.194	0.052	0.000012075
8.474	0.032	0.188	0.045	0.000010474
8.725	0.026	0.184	0.069	0.000008147
8.972	0.042	0.171	0.078	0.000008642
9.222	0.047	0.173	0.043	0.000006752
9.470	0.018	0.169	0.093	0.000004174
9.720	0.047	0.165	0.064	0.000004616