Electronic Supplementary Information

Switching nuclearity and Co(II) content through stoichiometry adjustment: $\{Co^{II}_6Co^{III}_3\}$ and $\{Co^{II}Co_4^{III}\}$ mixed valent complexes and their magnetic properties study

Alejandro V. Funes[a], Luca Carrella[b], Lorenzo Sorace[c], Eva Rentschler[b] and Pablo Alborés[a]*

[a] Departamento de Química Inorgánica, Analítica y Química Física/ INQUIMAE (CONICET), Facultad de Ciencias Exactas y Naturales Universidad de Buenos Aires, Pabellón 2, Ciudad Universitaria, C1428EHA Buenos Aires, Argentina
Fax: +5411 / 4576-3341
E-mail: albores@qi.fcen.uba.ar

[b] Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg - University of Mainz, Duesbergweg 10-14 D-55128 Mainz-Germany.
Fax: +49 6131 / 39-23922

[c] Dipartimento di Chimica "U. Schiff" and UdR INSTM, Università di Firenze, Via della Lastruccia 3, Polo Scientifico, 50019, Sesto Fiorentino, Firenze, Italy.
Fax: +39-055-4573372

Table S1. Crystallographic data of **1** and **2**.

	1	**2**
Empirical Formula	C_{68} H_{138} Co_9 N_3 O_{36}	C_{46} $H_{90.8}$ Co_5 N_5 O_{26}
Formula weight	2104.18	1424.68
T (K)	293 (2)	151 (1)
Crystal system	Triclinic	Monoclinic
Space Group	P-1	P21/n
a (Å)	14.7903 (15)	20.3316 (7)
b (Å)	15.2087 (12)	10.9609 (5)
c (Å)	25.894 (2)	28.8394 (12)
α (°)	91.970 (6)	90
β (°)	104.308 (8)	108.706 (4)
γ (°)	118.052 (9)	90
V (Å^3)	4903.1 (7)	6087.44
Z	2	4
D_{calc} (mg/m^3)	1.425	1.555
μ (mm^{-1})	1.558	1.418
F(000)	2196	2979
Crystal size (mm)	0.16 x 0.21 x 0.37	0.09 x 0.14 x 0.59
Crystal color/shape	purple blocks	red blocks
Radiation, graphite monochr.	Mo$K\alpha$, λ = 0.71073 Å	Mo$K\alpha$, λ = 0.71073 Å
θ Range data collection (°)	3.57 – 28.89	3.55 – 27.0
Index ranges	$-13 \le h \le 18$	$-24 \le h \le 25$
	$-19 \le k \le 19$	$-13 \le k \le 13$
	$-32 \le l \le 33$	$-36 \le l \le 35$
Reflections collected/unique	41016/20972(R_{int}=0.1092)	41683/13141(R_{int}=0.0713)
Observed reflections [$I>2\sigma(I)$]	9993	8733
Completeness (%)	99.1	97.9
Maximum / minimum transmission	1.000 / 0.548	1.000 / 0.819
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Weights, w	$1/[\sigma^2(F_o^2)+(0.1075P)^2+13.4587P]$ where $P=(F_o^2+2F_c^2)/3$	$1/[\sigma^2(F_o^2)+(0.0387P)^2+11.8423P]$ where $P=(F_o^2+2F_c^2)/3$
Data/restraints/parameters	20972/105/1098	13141/4/748
Goodness-of-fit (GOF) on F^2	1.028	1.053
Final R-index [$I>2\sigma(I)$] / all data	0.1010/ 0.1849	0.0624/ 0.1067
wR index [$I>2\sigma(I)$] /all data	0.2287/ 0.3027	0.1179/ 0.1387
Largest peak and hole (e A^{-3})	1.037 and -0.878	0.658 and -0.579

Table S2. Main bond angles (º) and distances (Å) of **1** and **2**.

1	
N17—Co4	1.965(5)
N15—Co1	1.981(4)
O11—Co1	1.912(3)
O19—Co2	2.360(3)
O19—Co3	1.896(4)
O19—Co1	1.892(3)
O25—Co2	2.041(3)
O25—Co1	1.872(3)
O110—Co5	1.884(4)
O110—Co4	1.879(3)
O28—Co5	1.867(4)
O28—Co4	1.921(4)
O27—Co4	1.887(3)
O27—Co2	2.031(4)
O23—Co4	1.915(3)
O15—Co3	1.901(3)
O15—Co1	1.870(4)
O16—Co3	1.878(4)
O26—Co2	2.036(4)
O26—Co3	1.898(3)
N16—Co3	1.964(4)
O21—Co3	1.914(3)
O22—Co1	1.916(4)
O14—Co5	1.916(4)
O18—Co5	1.869(3)
O18—Co2	2.004(4)
O13—Co5	1.933(3)
O47—Co4	1.890(4)
N18—Co5	1.978(6)
Co5—Co4	2.772(1)
Co3—Co1	2.7701(9)

Co2—O19—Co3	94.3(1)
Co2—O19—Co1	94.4(1)
Co3—O19—Co1	94.0(1)
Co2—O25—Co1	106.5(2)
Co5—O110—Co4	94.9(2)
Co5—O28—Co4	94.0(2)
Co4—O27—Co2	112.5(2)
Co3—O15—Co1	94.5(2)
Co2—O26—Co3	105.7(2)
Co5—O18—Co2	112.6(2)

2	
Co1—O32	1.95(1)
Co1—O2	1.978(8)
Co1—O10	1.959(6)
Co1—O30	1.98(1)
Co2—O13	2.14(1)
Co2—O16	2.03(1)
Co2—O14	2.098(9)
Co2—O2	2.133(8)
Co2—O1	2.045(5)
Co2—O33	2.289(8)
Co3—O1	2.050(8)
Co3—O5	2.002(5)
Co3—O18	2.07(1)
Co3—O17	2.020(8)
Co3—O15	2.024(8)
Co4—O20	1.914(9)
Co4—O5	1.843(7)
Co4—O19	1.891(8)
Co4—O7	1.952(6)
Co4—N2	1.961(9)
Co4—O6	1.876(6)
Co5—O34	1.892(7)
Co5—O22	1.891(6)
Co5—N3	1.98(1)
Co5—O21	1.941(9)
Co5—O7	1.894(5)
Co5—O6	1.929(7)
Co6—O29	2.049(8)
Co6—O2	2.101(7)
Co6—O1	2.068(8)
Co6—O4	2.081(5)
Co6—O9	2.256(8)
Co6—O3	2.116(6)
Co7—O24	2.100(8)
Co7—O8	2.157(9)
Co7—O23	2.022(7)
Co7—O34	2.054(8)
Co7—O4	2.063(6)
Co7—O3	2.097(6)
Co8—O26	2.200(8)
Co8—O27	2.115(8)
Co8—O9	2.134(6)
Co8—O4	1.997(7)
Co8—O8	2.252(8)
Co8—O28	2.039(9)
Co9—O10	1.890(7)
Co9—O8	1.903(7)

Co9—O9	1.894(7)
Co9—O3	1.899(8)
Co9—N1	1.91(1)
Co9—O25	1.910(8)
Co2—Co6	3.070(2)
Co4—Co5	2.837(2)
Co6—Co8	3.008(2)
Co7—Co9	2.893(3)

Co2—O1—Co3	110.2(3)
Co2—O1—Co6	96.5(3)
Co3—O1—Co6	134.4(3)
Co1—O10—Co9	121.9(4)
Co1—O2—Co2	113.1(4)
Co1—O2—Co6	114.9(4)
Co2—O2—Co6	92.9(3)
Co6—O3—Co7	99.8(3)
Co6—O3—Co9	101.5(3)
Co7—O3—Co9	92.6(3)
Co5—O34—Co7	118.0(3)
Co6—O4—Co7	102.1(3)
Co6—O4—Co8	95.0(2)
Co7—O4—Co8	105.2(3)
Co3—O5—Co4	109.9(3)
Co4—O6—Co5	96.4(3)
Co4—O7—Co5	95.1(3)
Co7—O8—Co8	94.0(3)
Co7—O8—Co9	90.7(3)
Co8—O8—Co9	99.6(3)
Co6—O9—Co8	86.5(2)
Co6—O9—Co9	96.8(3)
Co8—O9—Co9	104.2(3)

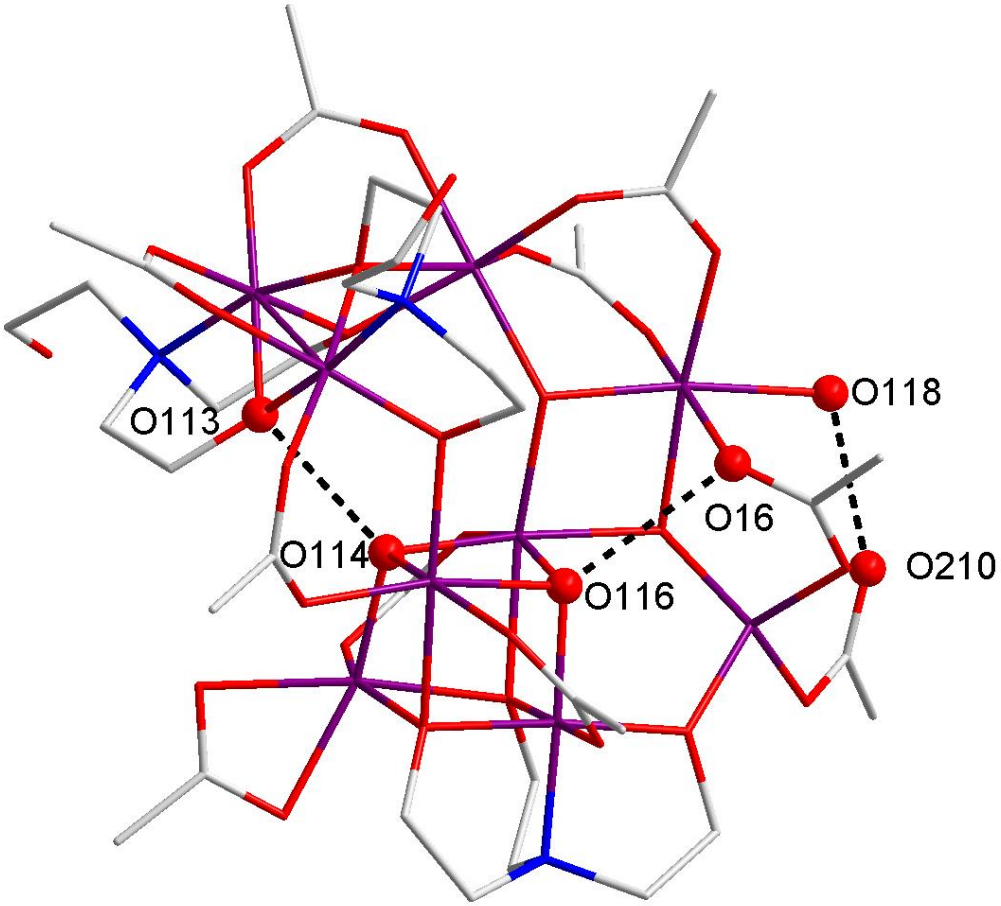

Figure ESI1. Intra-molecular H-bonding interactions in compound **1** structure. Hydrogen atoms and tert-butyl groups have been omitted for sake of clarity. Atoms colours code: violet: cobalt; red: oxygen; blue: nitrogen and gray: carbon.

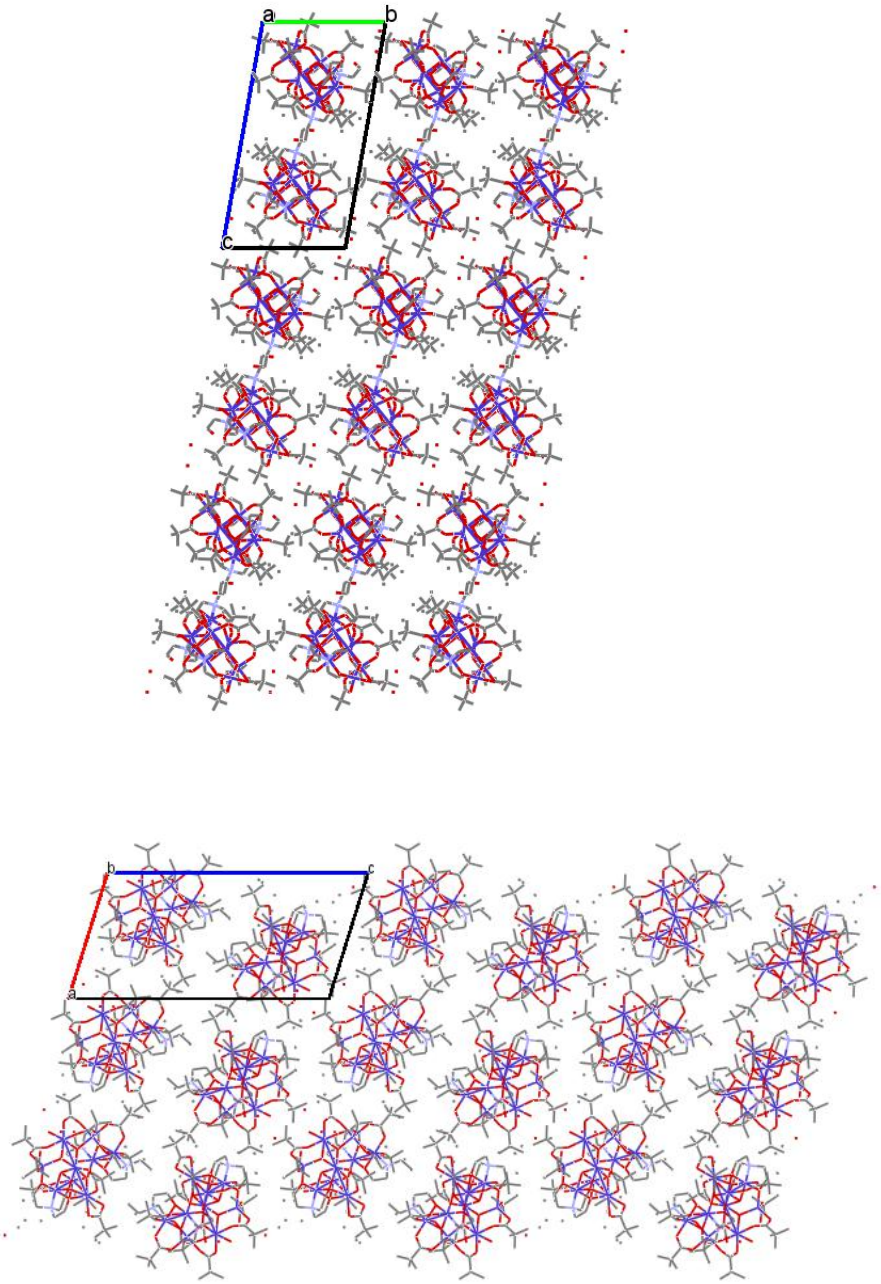

Figure ESI2. Crystal packing views of compound **1**. Top: *a*-axis direction; Bottom: *b*-axis direction. Hydrogen atoms have been omitted for sake of clarity.

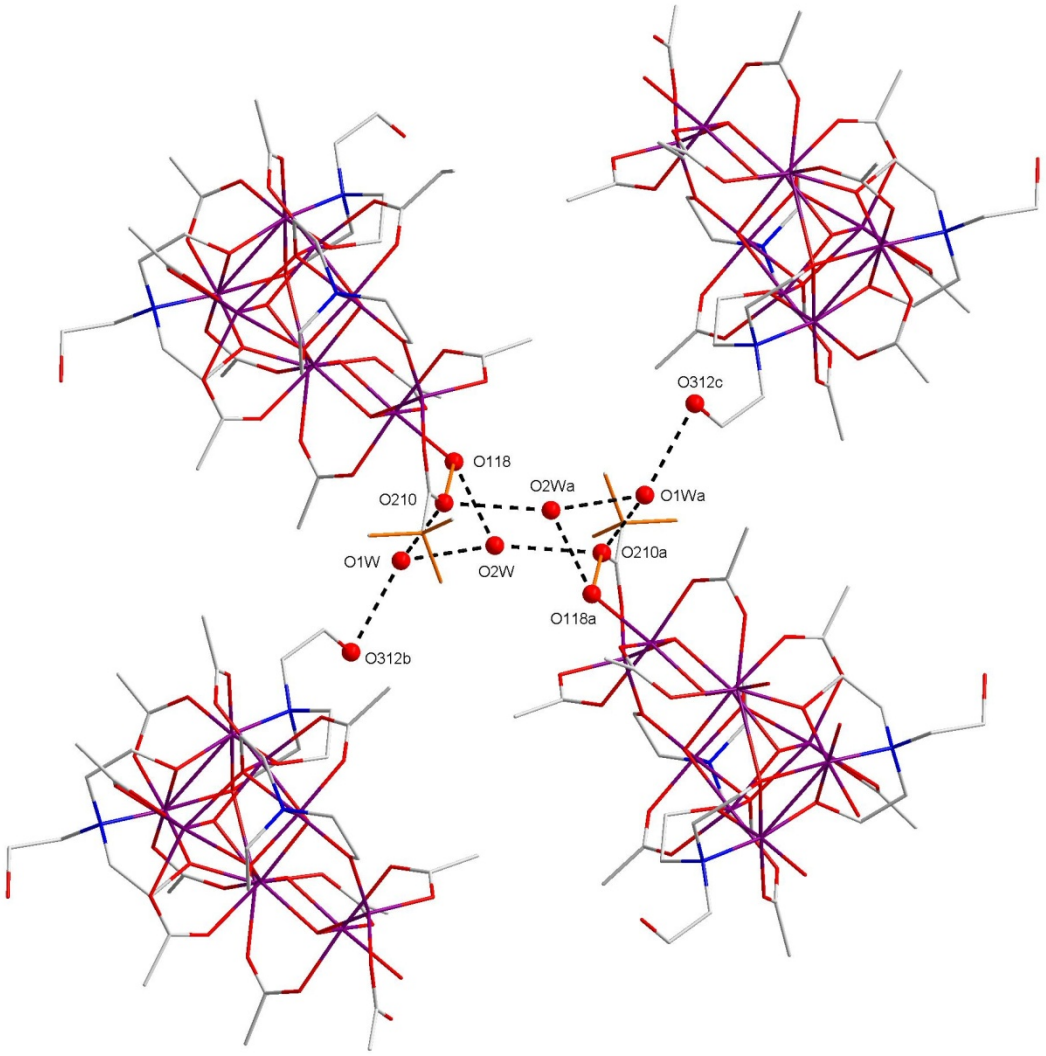

Figure ESI3. Inter-molecular H-bonding interactions in compound **1** structure. Hydrogen atoms and tert-butyl groups have been omitted for sake of clarity. Atoms colours code: violet: cobalt; red: oxygen; blue: nitrogen and gray: carbon. Symmetry codes, a: -x, -y, -z; b: x, -1+y, z; c: -x, 1-y, z.

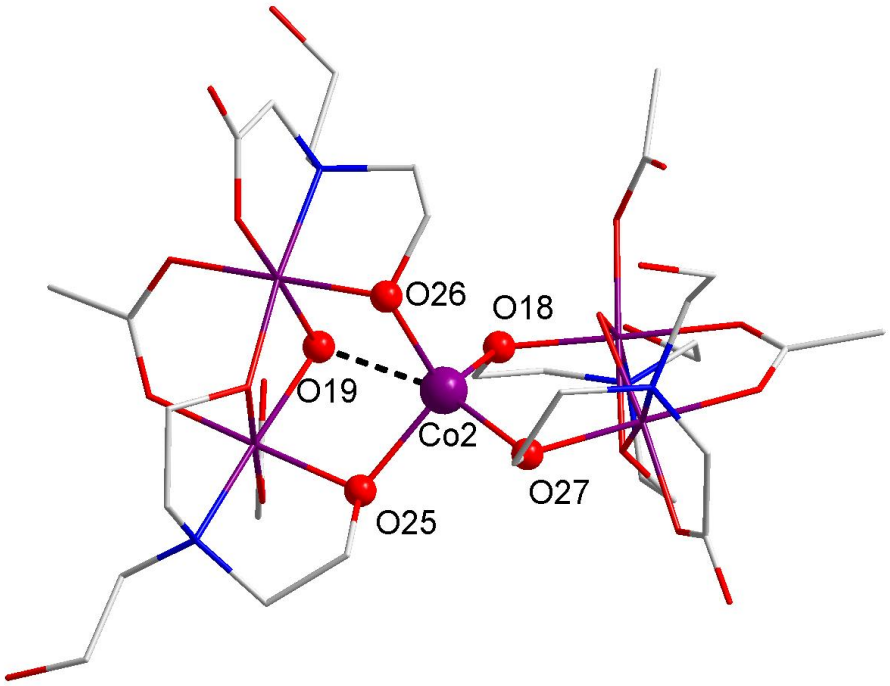

Figure ESI4. Molecular representation of the tetrahedral environment of Co(II) ion in compound **2,** remarking the short contact Co2-O19 distance. Hydrogen atoms and tert-butyl groups have been omitted for sake of clarity. Atoms colours code: violet: cobalt; red: oxygen; blue: nitrogen and gray: carbon.

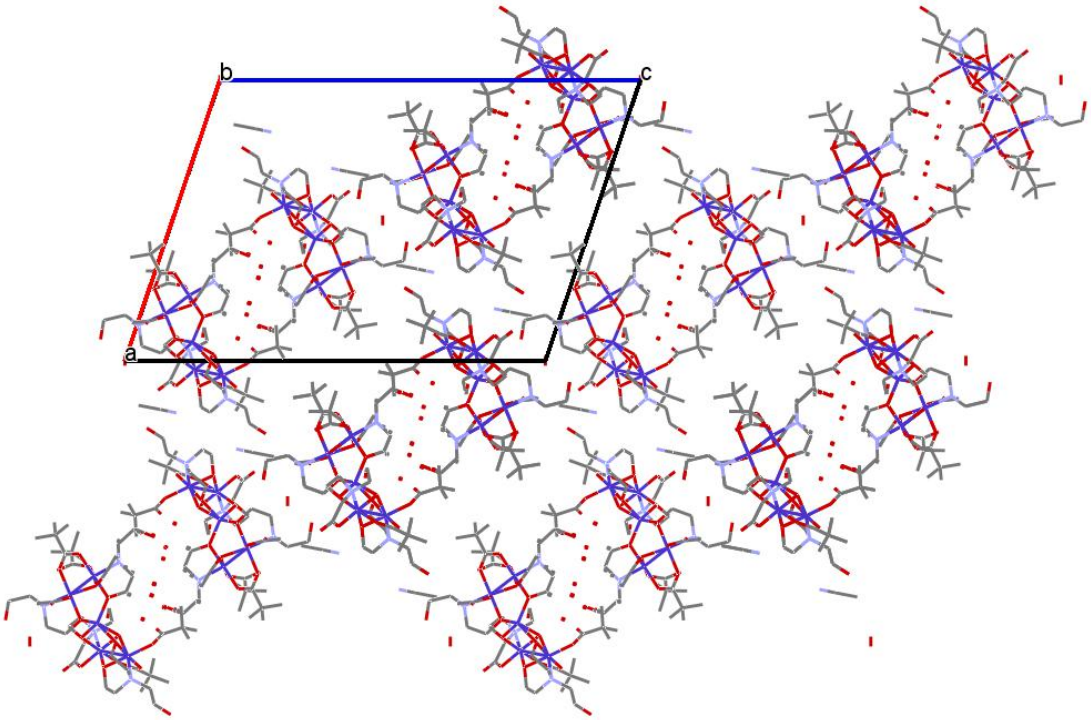

Figure ESI5. Crystal packing view of compound **2** along *b*-axis direction. Hydrogen atoms have been omitted for sake of clarity.

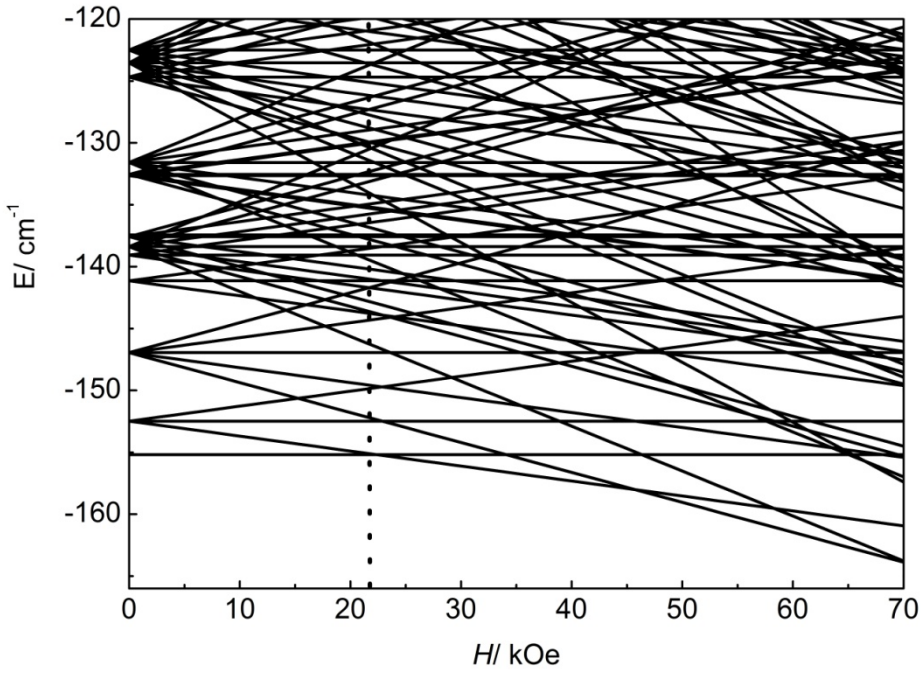

Figure ESI6. Low lying spin multiplet energy level plot arising from best fitting parameters of compound **1**. The dotted line remarks the level crossing field.

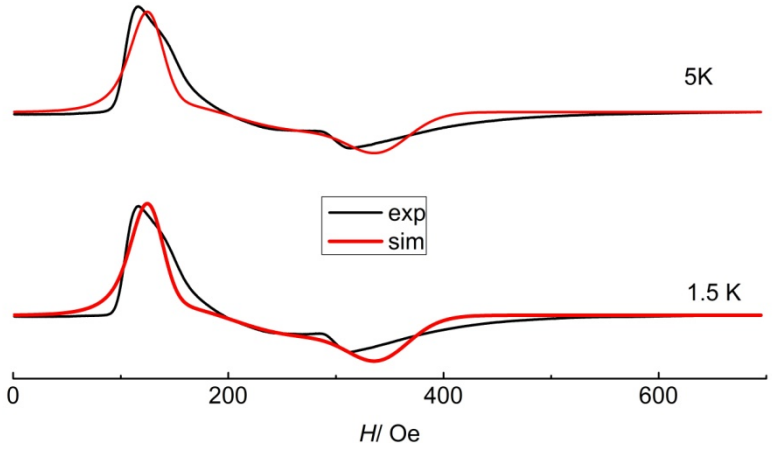

Figure ESI7. Powder X-band EPR spectra at 1.5 and 5 K of compound **2** as S_{eff}=1/2. Simulation linewidth: 260 Oe; *g*-strain: [0,0.3,0.3]; *H*-strain/ Oe: [0, 2300, 210].

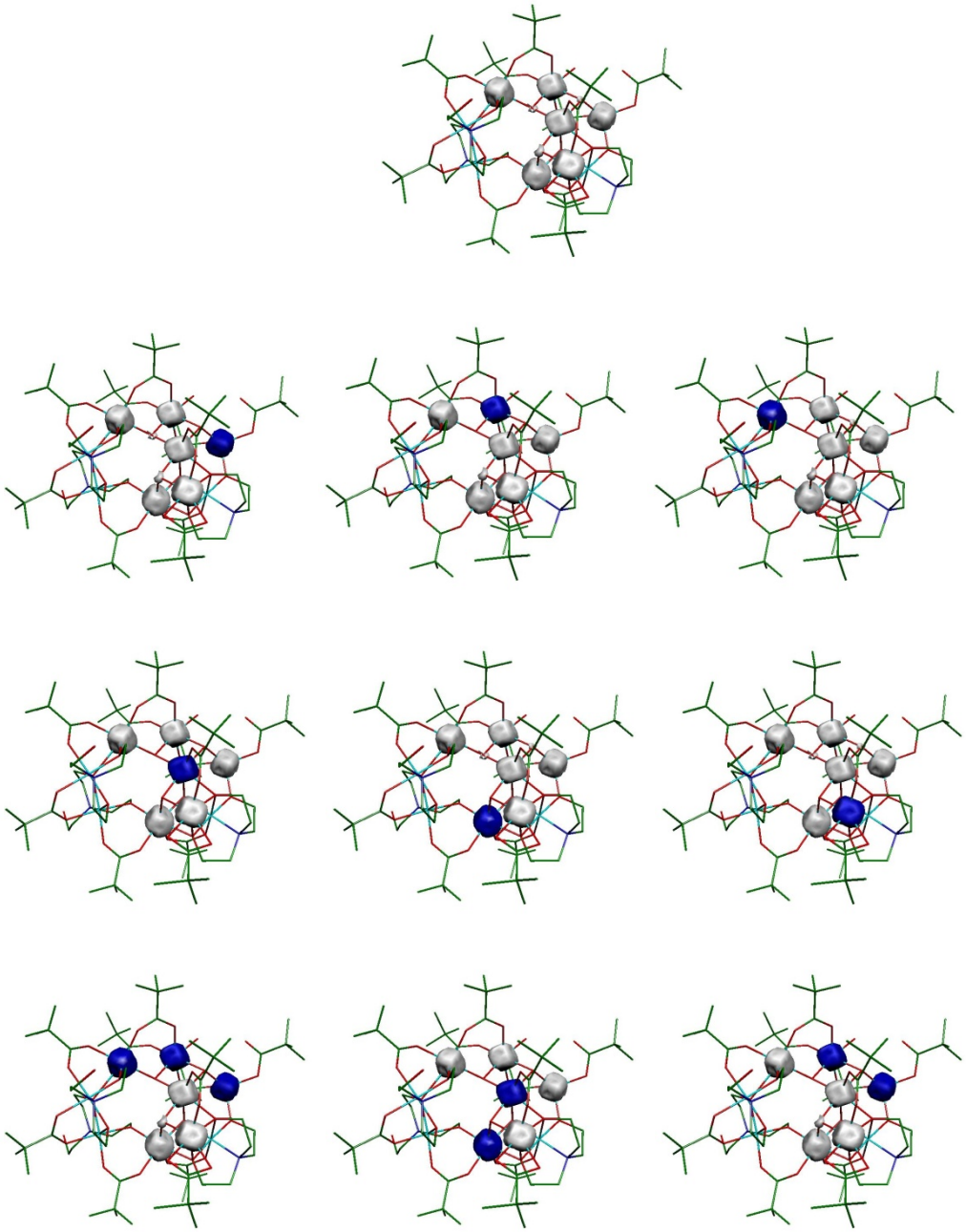

Figure ESI8. Spin density (isosurface: 0.03 a.u.; white: positive; blue: negative) of the different single-determinant configurations calculated for the extraction of the exchange coupling constant values. First line: HS state; From top-bottom and left-right: BS1 to BS9 states respectively.

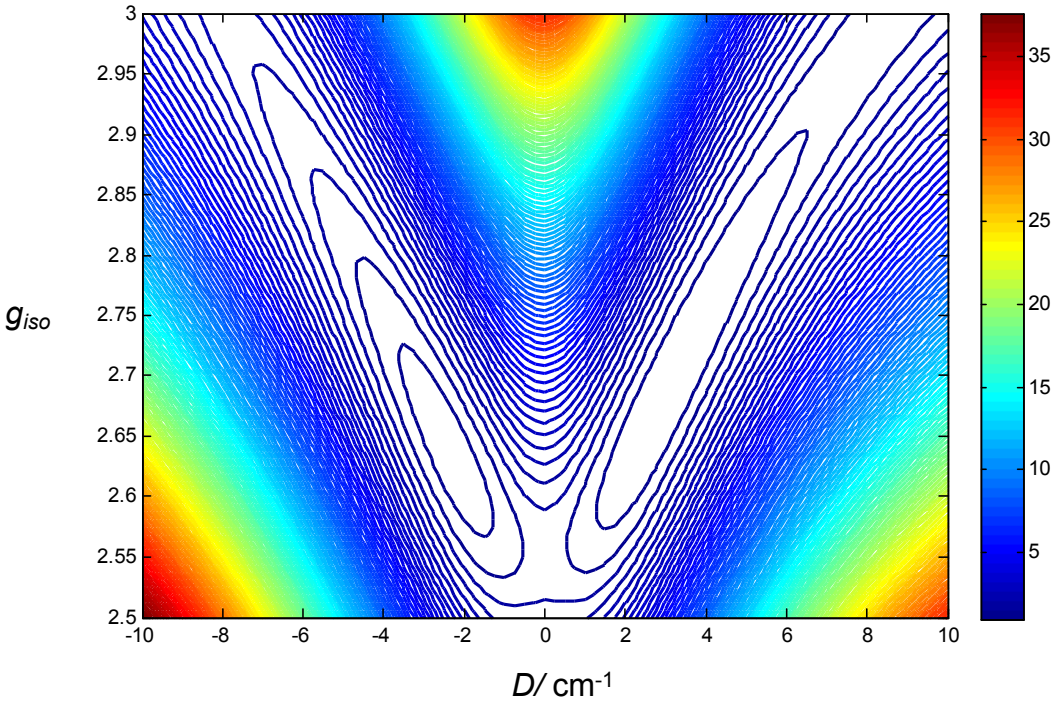

Figure ESI9. *D* vs *g* error surface contour plot from magnetization data simulations of compound **2**.

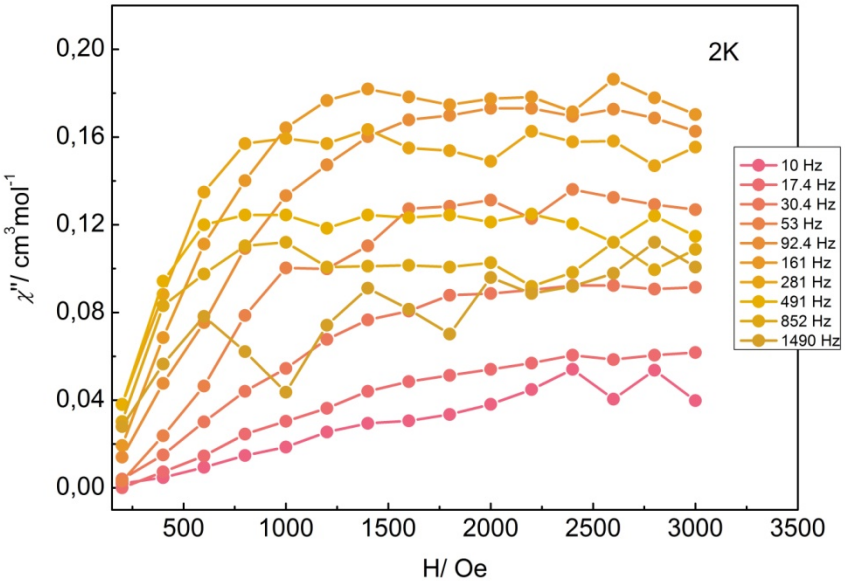

Figure ESI10. Compound **2** χ_m'' vs external applied H_{DC}, 0-1500 Hz (driving field 3 Oe) plot, at 2-K .

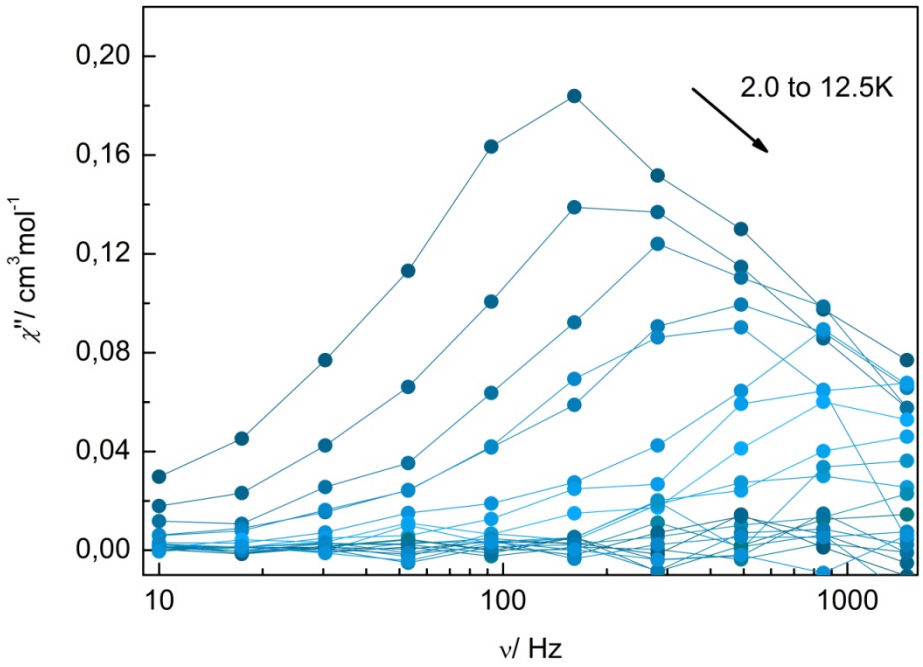

Figure ESI11. Compound **2** χ_m'' vs driving frequency (logarithmic scale), 0-1500 Hz (driving field 3 Oe) plot, in the range 2-12.5 K under a 1400 Oe DC applied field.

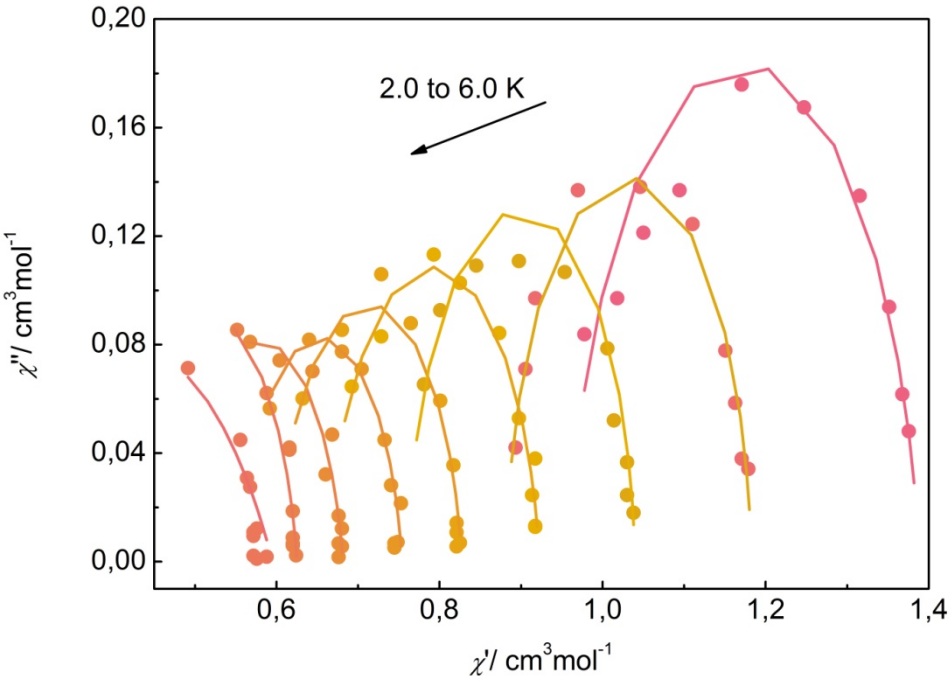

Figure ESI12. Cole-Cole plot at 2600 Oe DC applied field of compound **2**, in the 2-6 K range. Circles: experimental data; Lines: best fitting (see Text).

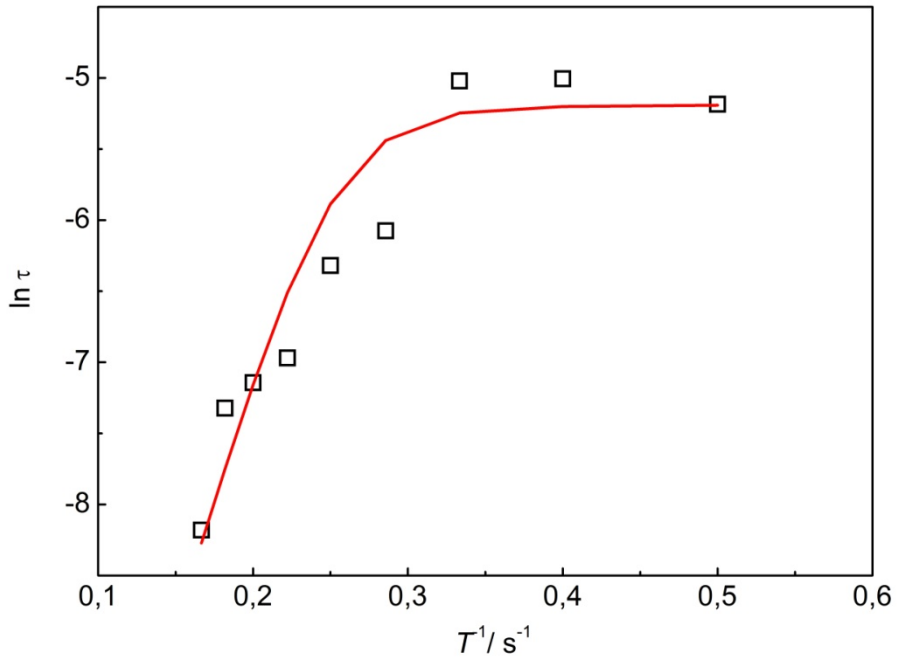

Figure ESI13. Arrhenius type plot for the *T* dependence of the characteristic relaxation time at 1400 Oe DC external field for compound **2**. Squares: experimental data; Full lines: best fitting curves (see Text).