SUPPLEMENTARY MATERIALS

New Syntheses, Analytic Spin Hamiltonians, Structural and Computational Characterization for a Series of tri-, hexa- and hepta-nuclear Copper (II) Complexes with Prototypic Patterns.

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X-ray diffraction for compounds **1-3**

Table S1. Crystal data for complexes **1-3**.

Compound	**1**	**2**	**3**
Formula	$C_{19}H_{24}Cu_3N_9O_{16}$	$C_{94}H_{114}Cu_6N_{30}O_{20}$	$C_{48}H_{74}Cu_7N_{18}O_{32}$
Formula weight	825.09	2365.38	1860.04
Temperature, K	293	293	293
Crystal system	orthorhombic	trigonal	trigonal
Space group	Pbca	R-3	R-3c
a, Å	28.2869(19)	20.826(3)	18.893(1)
b, Å	26.1979(14)	20.826(3)	18.893(1)
c, Å	18.7913(10)	22.2759(16)	35.431(3)
α, ◦	90	90	90
β, ◦	90	90	90
γ, ◦	90	120	120
V, $Å^3$	13925.4(14)	8367.2(18)	10952(2)
Z	16	3	6
Dcalc, Mg/m^3	1.574	1.414	1.692
F(000)	6656.00	3703.9	5682.0
μ(Mo Kα), mm−1	1.892	1.200	2.096
Range(2θ), deg	6.06 to 54.98	6.26 to 54.96	6.6 to 54.9
Independent reflections	12870	4258	2801
Data/restraints/parameters	12870/0/848	4258/0/246	2801/0/161
Final R indices [I > 2σ(I)]	0.1255	0.0774	0.0553
R indices (all data)	0.2718	0.1229	0.0914
Goodness-of-fit on F^2	1.028	1.124	1.056

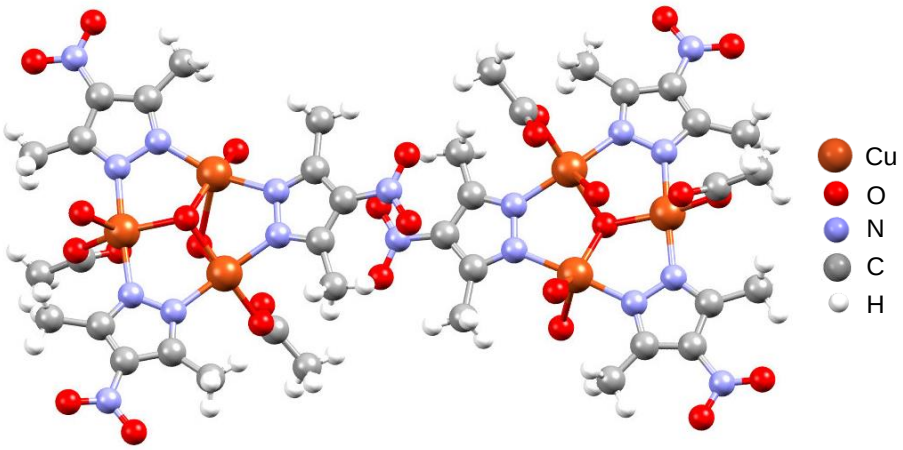

Figure S1. X-ray molecular structure of compound **1** with atoms coloring scheme. The solvent molecules were omitted for clarity.

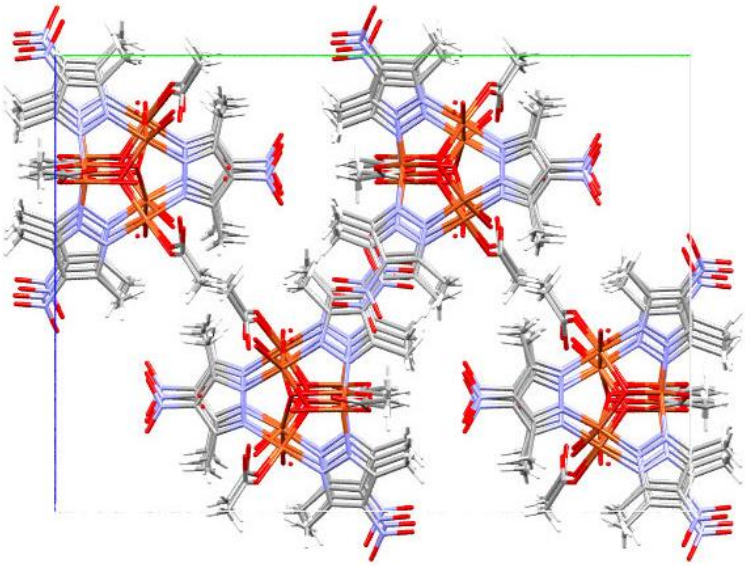

Figure S2. Packing along *a* axis for compound **1**, (representation with Mercury and POV-Ray).

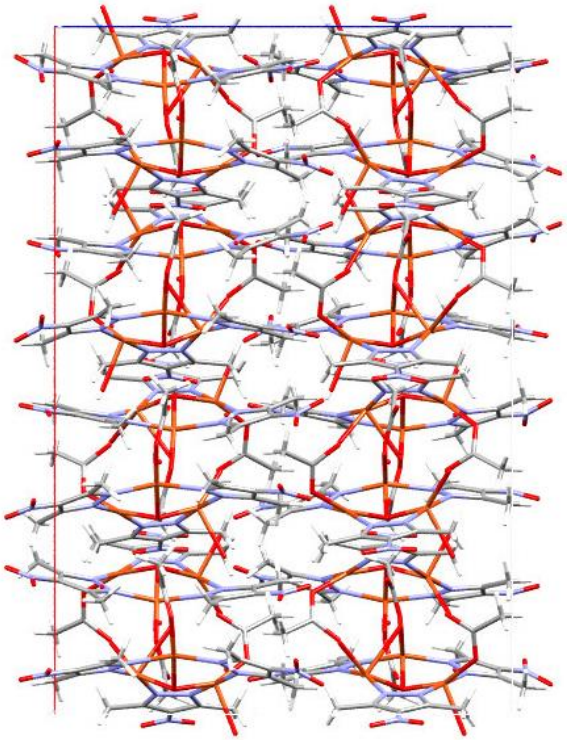

Figure S3. Packing along *b* axis for compound **1**, (representation with Mercury and POV-Ray).

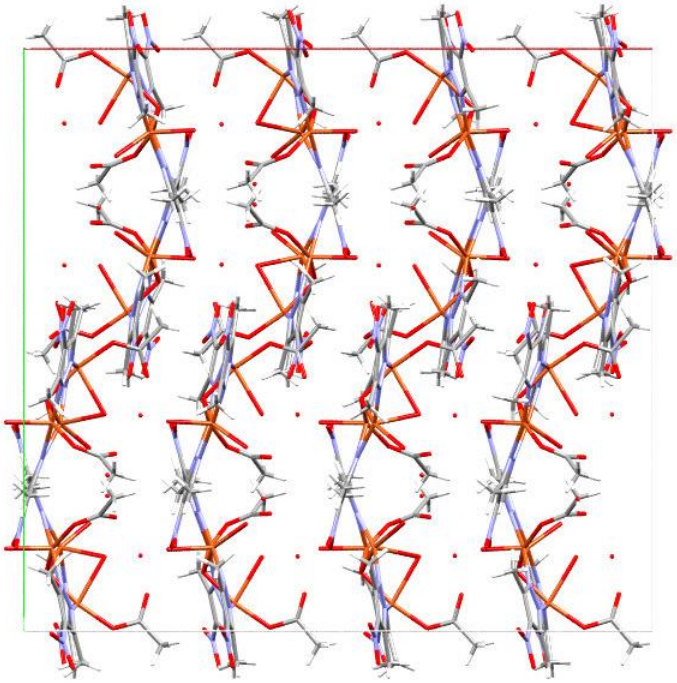

Figure S4. Packing along *c* axis for compound **1**, (representation with Mercury and POV-Ray).

Table S2. Selected bond lengths [Å] and angles [°] for **1**.

Atoms	Bond lengths, Å	Atoms	Bond angles, °
Cu1-O1	1.974(9)	O1-Cu1-O10	169.6(4)
Cu1-O10	1.942(10)	O1-Cu1-N1	88.6(4)
Cu1-N1	1.948(11)	O1-Cu1-N8	88.8(4)
Cu1-N8	1.984(12)	O10-Cu1-N1	92.1(4)
Cu2-O1	2.039(8)	O10-Cu1-N8	94.8(5)
Cu2-O8	2.037(10)	N1-Cu1-N8	155.9(5)
Cu2-O9	2.267(11)	O1-Cu2-O8	142.8(4)
Cu2-N2	1.959(12)	O1-Cu2-O9	100.2(4)
Cu2-N4	1.939(13)	O1-Cu2-N2	90.9(4)
Cu3-O1	1.985(8)	O1-Cu2-N4	90.2(5)
Cu3-O12	1.936(12)	O8-Cu2-O9	117.0(4)
Cu3-N5	1.948(13)	N2-Cu2-N4	175.9(5)
Cu3-N7	1.970(12)	O1-Cu3-O12	163.5(4)
		O1-Cu3-N5	89.8(5)
		O1-Cu3-N7	88.4(4)
		O12-Cu3-N5	93.3(5)
		O12-Cu3-N7	91.3(5)
		N5-Cu3-N7	169.4(5)

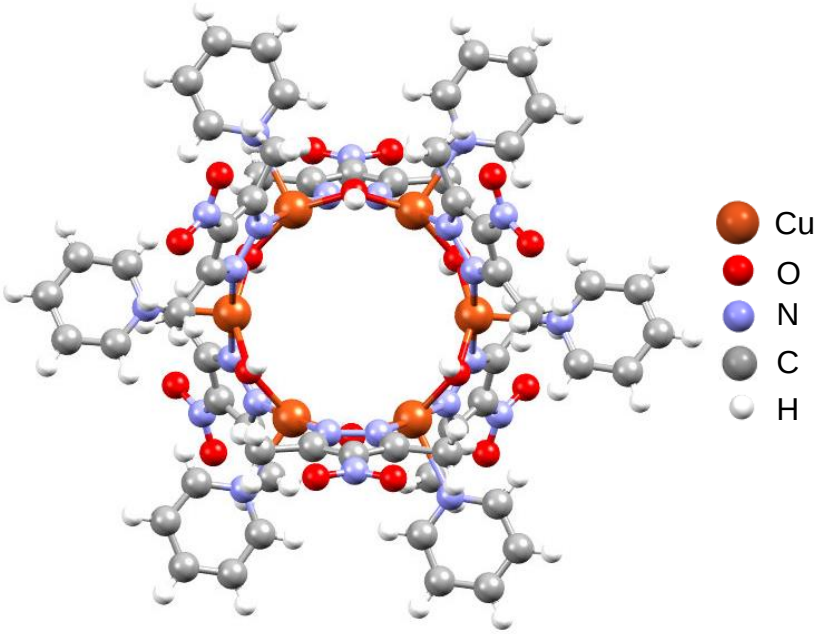

Figure S5. X-ray molecular structure of compound **2** with atoms coloring scheme. The solvent molecules were omitted for clarity.

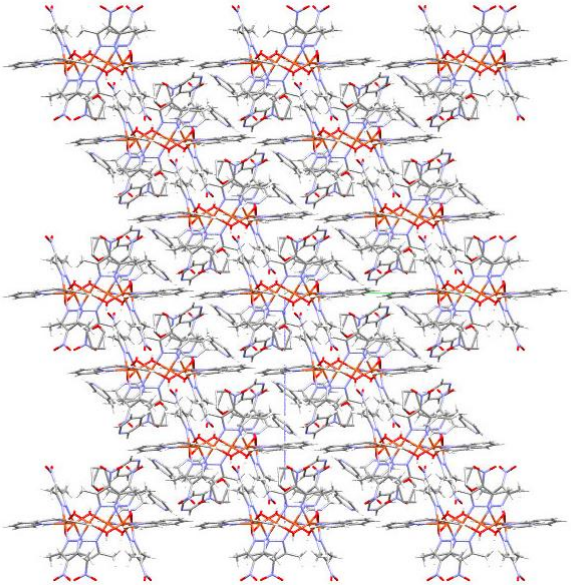

Figure S6. Packing along *a* axis for compound **2**, (representation with Mercury and POV-Ray).

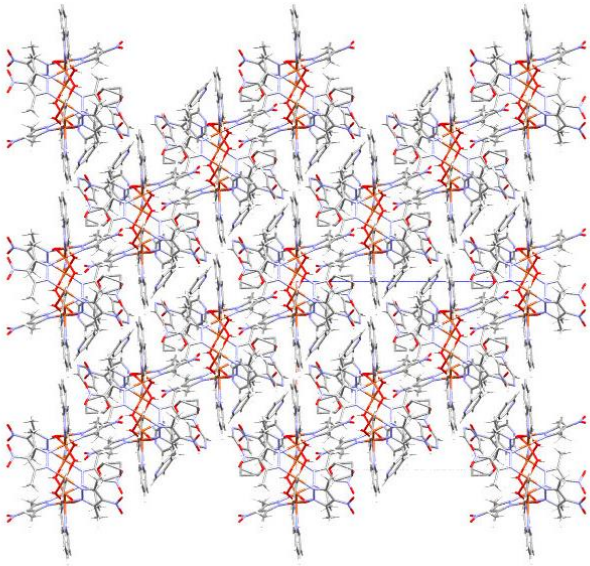

Figure S7. Packing along *b* axis for compound **2**, (representation with Mercury and POV-Ray).

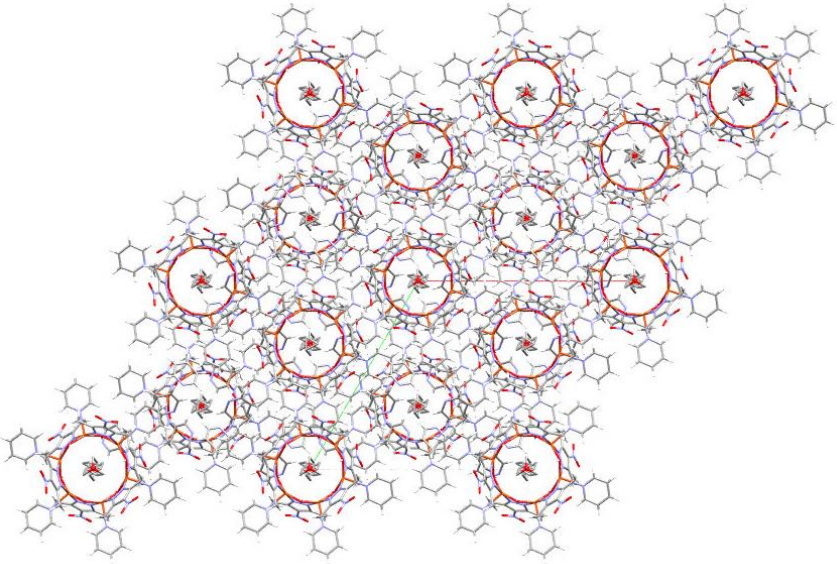

Figure S8. Packing along *c* axis for compound **2**, (representation with Mercury and POV-Ray).

Table S3. Selected bond lengths [Å] and angles [°] for **2**.

Atoms	Bond lengths, Å	Atoms	Bond angles, °
Cu1-N1	2.018(4)	N2-Cu1-N1	178.67(17)
Cu1-N2	2.003(4)	O1-Cu1-N1	93.99(16)
Cu1-O1	1.947(4)	O1-Cu1-N2	85.91(16)
Cu1- N4	2.359(5)	N4-Cu1-N1	92.06(16)
Cu1-O1[1]	1.943(4)	N4-Cu1-N2	89.26(17)
N1-N2[1]	1.397(6)	N4-Cu1-O1	100.45(18)
		N4-Cu1-O1[1]	107.31(18)
		N2[1]-N1-Cu1	118.0(3)
		N1[2]-N2-Cu1	119.3(3)

[1]-1/3+Y,1/3-X+Y,4/3-Z; [2]2/3-Y+X,1/3+X,4/3-Z; [3]1-Y,+X-Y,+Z; [4]1+Y-X,1-X,+Z

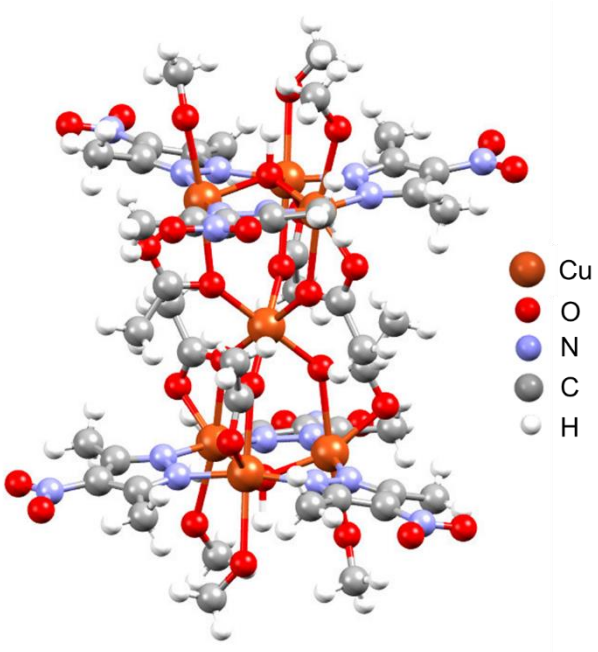

Figure S9. X-ray molecular structure of compound **3** with atoms coloring scheme.

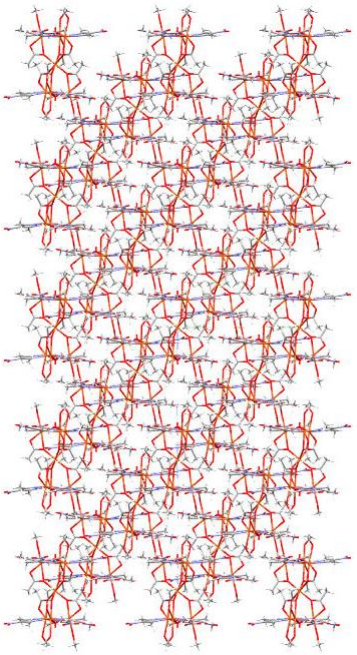

Figure S10. Packing along *a* axis for compound **3**, (representation with Mercury and POV-Ray).

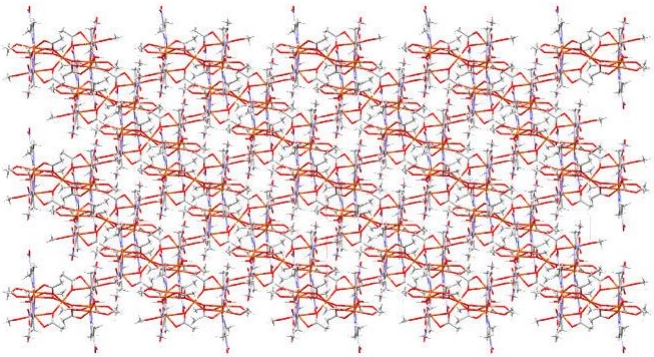

Figure S11. Packing along *b* axis for compound **3**, (representation with Mercury and POV-Ray).

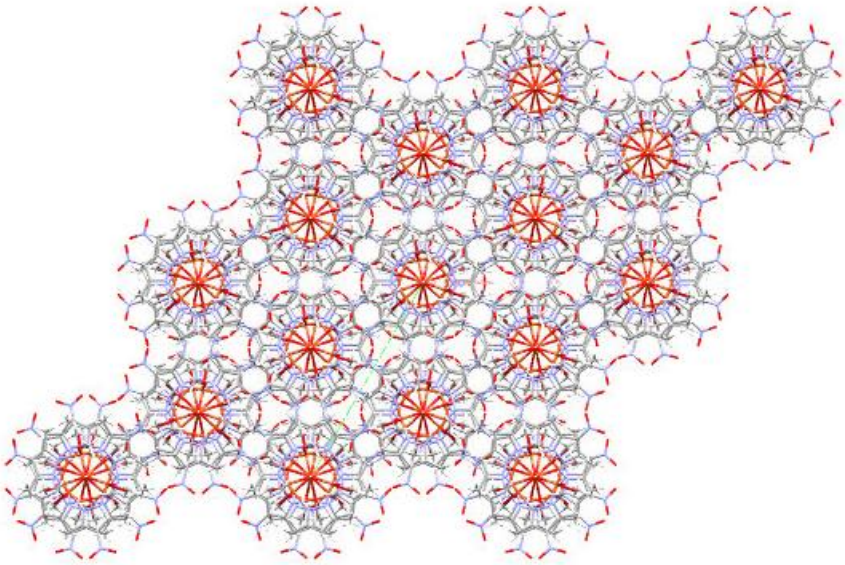

Figure S12. Packing along *c* axis for compound **3**, (representation with Mercury and POV-Ray).

Table S4. Selected bond lengths [Å] and angles [°] for **3**.

Atoms	Bond lengths, Å	Atoms	Bond angles, °
Cu1-O1	2.056(4)	O1-Cu1-O1[1]	85.06(15)
Cu1-O1[1]	2.054(4)	O1-Cu1-O1[3]	179.95(13)
Cu1-O1[2]	2.055(4)	O1-Cu1-O1[4]	94.86(15)
Cu1-O1[3]	2.053(4)	O1[1]-Cu1-O1[5]	94.94(15)
Cu1-O1[4]	2.054(4)	O2-Cu2-O3	158.05(18)
Cu1-O1[5]	2.053(4)	O2-Cu2-N1	92.52(17)
Cu2-O2	2.014(4)	O3-Cu2-N1	90.31(12)
Cu2-O3	2.0055(18)	N1-Cu2-N2[1]	169.82(16)
Cu2-N1	1.991(5)	Cu1-O1-C1	143.1(4)
Cu2-N21	1.971(6)	Cu2-O2-C1	101.6(4)
		Cu2-O3-Cu2[1]	110.99(14)
		Cu2-O3-Cu2[2]	110.93(14)
		Cu2[1]-O3-Cu2[2]	111.00(14)
		Cu2-N1-N2	117.1(4)
		Cu2-N1-C4	133.5(3)
		N2-N1-C4	108.6(4)
		Cu2[2]-N2-N1	120.0(4)
		Cu2[2]-N2-C6	131.3(3)

[1] -Y+1,X-Y+1,Z; [2]-X+Y,-X+1,Z; [3]-X+2/3,-Y+1/3+1,-Z+1/3+1;[4] Y+2/3-1,-X+Y+1/3,-Z+1/3+1;

[5] X-Y+2/3,X+1/3,-Z+1/3+1

Table S5. The count and energies of spin states (including total and intermediate spin quantum numbers) in a copper hexanuclear system, constituted as dimer of trimers, with the topology discussed in the main text.

S	S_{123}	S_{456}	$E(S,S_{123},S_{456})$
0	1/2	1/2	0
0	1/2	1/2	0
0	1/2	1/2	0
0	1/2	1/2	0
0	3/2	3/2	$-6J+6j$
1	1/2	1/2	$-2j$
1	1/2	1/2	$-2j$
1	1/2	3/2	$-3J+j$
1	1/2	1/2	$-2j$
1	1/2	1/2	$-2j$
1	1/2	3/2	$-3J+j$
1	3/2	1/2	$-3J+j$
1	3/2	1/2	$-3J+j$
1	3/2	3/2	$-6J+4j$
2	1/2	3/2	$-3J-3j$
2	1/2	3/2	$-3J-3j$
2	3/2	1/2	$-3J-3j$
2	3/2	1/2	$-3J-3j$
2	3/2	3/2	$-6J$
3	3/2	3/2	$-6J-6j$

Table S6. Numeric energies in a hexanuclear system with local 1/2 spin centres and hexagonal topology (having unique exchange coupling parameter J along the edges).

#	S	HDvV
1	0	0
2	0	-2.60555 J
3	0	-4.60555 J
4	0	-4.60555 J
5	0	-7.21110 J
6	1	-1.36948 J
7	1	-4.16710 J
8	1	-4.16710 J
9	1	-3.60555 J
10	1	-3.60555 J
11	1	-5.84162 J
12	1	-6.60555 J
13	1	-7.16710 J
14	1	-7.16710 J
15	2	-4.60555 J
16	2	-5.60555 J
17	2	-5.60555 J
18	2	-7.60555 J
19	2	-7.60555 J
20	3	-8.60555 J

Table S7. The count and energies of spin states in a copper heptanuclear system, constituted as a central atom interacting equivalently with two trimers, having mutually the same parameterization as convened in the hexameric system from Table S5.

S	$S_{1\text{-}6}$	S_{123}	S_{456}	$E(S, S_{1\text{-}6}, S_{123}, S_{456})$
1/2	0	1/2	1/2	0
1/2	0	1/2	1/2	0
1/2	0	1/2	1/2	0
1/2	0	1/2	1/2	0
1/2	1	1/2	1/2	$2J'-2j$
1/2	1	1/2	1/2	$2J'-2j$
1/2	1	1/2	3/2	$-3J+2J'+j$
1/2	1	1/2	1/2	$2J'-2j$
1/2	1	1/2	1/2	$2J'-2j$
1/2	1	1/2	3/2	$-3J+2J'+j$
1/2	1	3/2	1/2	$-3J+2J'+j$
1/2	1	3/2	1/2	$-3J+2J'+j$
1/2	0	3/2	3/2	$-6J+6j$
1/2	1	3/2	3/2	$-6J+2J'+4j$
3/2	1	1/2	1/2	$-J'-2j$
3/2	1	1/2	1/2	$-J'-2j$
3/2	1	1/2	3/2	$-3J-J'+j$
3/2	2	1/2	3/2	$-3J+3J'-3j$
3/2	1	1/2	1/2	$-J'-2j$
3/2	1	1/2	1/2	$-J'-2j$
3/2	1	1/2	3/2	$-3J-J'+j$
3/2	2	1/2	3/2	$-3J+3J'-3j$
3/2	1	3/2	1/2	$-3J-J'+j$
3/2	2	3/2	1/2	$-3J+3J'-3j$
3/2	1	3/2	1/2	$-3J-J'+j$
3/2	2	3/2	1/2	$-3J+3J'-3j$
3/2	1	3/2	3/2	$-6J-J'+4j$
3/2	2	3/2	3/2	$-6J+3J'$
5/2	2	1/2	3/2	$-3J-2J'-3j$
5/2	2	1/2	3/2	$-3J-2J'-3j$
5/2	2	3/2	1/2	$-3J-2J'-3j$
5/2	2	3/2	1/2	$-3J-2J'-3j$
5/2	2	3/2	3/2	$-6J-2J'$
5/2	3	3/2	3/2	$-6J+4J'-6j$
7/2	3	3/2	3/2	$-6J-3J'-6j$

Table S8. The high spin (HS) and broken symmetry (BS) energies calculated for compond **1** gived as absolute and relative energies to those of highest spin. The solution, calculated vs. fit to model, is exact with J_{12}=-144.9 cm^{-1}, J_{13}=-142.7 cm^{-1} and J_{23}=-114.3 cm^{-1}.

Name	ΔE(BSi) General Formulas	Absolute Energy (a.u.)	$\langle S^2 \rangle$	Relative Energy Calc. & Fit (cm^{-1})
HS	0	-7130.80765	3.756	0
BS1	$J_{12}+J_{13}$	-7130.80896	1.729	-287.6
BS2	$J_{12}+J_{23}$	-7130.80883	1.727	-259.2
BS3	$J_{13}+J_{23}$	-7130.80882	1.728	-257.0

Table S9. The high spin (HS) and broken symmetry (BS) energies calculated for compond **2** gived as absolute and relative energies to those of highest spin. The fit value is J=-240.4 cm^{-1}.

Name	ΔE(BSi) General Formulas	Absolute Energy (a.u.)	$\langle S^2 \rangle$	Rel, Energy Calc.(cm^{-1})	Rel. Energy Fit (cm^{-1})
HS	0	-14833.30792	12.011	0	0
BS1	2J	-14833.31011	6.972	-480.6	-480.8
BS12	2J	-14833.31012	3.972	-482.0	-480.8
BS13	4J	-14833.31230	3.934	-960.2	-961.6
BS14	4J	-14833.31230	3.933	-961.0	-961.6
BS123	2J	-14833.31012	2.972	-481.9	-480.8
BS124	4J	-14833.31230	2.933	-961.5	-961.6
BS135	6J	-14833.31448	2.896	-1439.0	-1442.4

Table S10. The high spin (HS) and broken symmetry (BS) energies calculated for compond **3** gived as absolute and relative energies to those of highest spin. The fit corresponds to the following parameters: J=-162.3 cm^{-1}, J'=+4.9 cm^{-1} and j= +0.75 cm^{-1}.

Name	ΔE(BSi) General Formulas	Absolute Energy (a.u.)	$\langle S^2 \rangle$	Rel. Energy Calc. (cm^{-1})	Rel. Energy Fit (cm^{-1})
HS	0	-16746.67162	15.799		
BS1	6J'	-16746.67317	9.761	27.7	24.0
BS2	2J+J'+3j	-16746.67308	9.734	-313.9	-318.4
BS12	2J+5J'+3j	-16746.67316	5.735	-294.3	-302.4
BS23	2J+2J'+6j	-16746.67462	5.736	-312.1	-312.1
BS25	4J+2J'+4j	-16746.67468	5.705	-631.8	-638.2
BS26	4J+2J'+4j	-16746.67478	5.705	-643.8	-638.2