Supplementary Information

Anisotropic exchange interaction and field-induced SMM behaviour in a mixed valence $\{Co^{II}_4Co^{III}_2\}$ complex

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Table SI1. Best fitting parameters of complex **1** AC susceptibility data at 1500 Oe according to the generalized Debye model.

T/ K	χ_S/cm^{3}mol^{-1}	χ_T/cm^{3}mol^{-1}	α	τ/ s
2.00	0.257	0.777	0.374	9.44E-05
2.16	0.203	0.766	0.466	6.18E-05
2.34	0.214	0.738	0.463	5.11E-05
2.53	0.202	0.722	0.501	4.02E-05
2.73	0.217	0.669	0.471	2.77E-05
2.95	0.260	0.628	0.425	2.58E-05
3.19	0.243	0.612	0.477	1.75E-05
3.45	0.278	0.594	0.484	1.89E-05

Table SI2. Best fitting parameters of complex **1** AC susceptibility data at 3000 Oe according to the generalized Debye model.

T/ K	χ_S/cm^{3}mol^{-1}	χ_T/cm^{3}mol^{-1}	α	τ/ s
2.00	0.161	0.681	0.575	7.91E-04
2.16	0.181	0.628	0.534	5.13E-04
2.34	0.144	0.656	0.608	4.03E-04
2.53	0.185	0.644	0.589	4.23E-04
2.73	0.039	0.652	0.701	8.04E-05
2.95	0.212	0.614	0.594	2.89E-04
3.19	0.000	0.701	0.795	2.32E-05
3.45	0.234	0.582	0.609	2.07E-04

Table SI3. Complex **1** energy spectrum and *g* tensors of exchange states as arising from experimental magnetization data and *ab-initio* calculations. Possible pseudo doublets assignments are remarked in bold type.

Exp cm^{-1}	***g*-tensors** g_x,g_y,g_z	$J_1 < 0$ $J_2 < 0$ cm^{-1}	***g*-tensors** g_x,g_y,g_z	$J_1 < 0$ $J_2 > 0$ cm^{-1}	***g*-tensors** g_x,g_y,g_z	$J_1 > 0$ $J_2 < 0$ cm^{-1}	***g*-tensors** g_x,g_y,g_z
0.0	0.0 0.0 0.0	0.0	-	0.0	-	0.0	-
0.0		6.0	-	11.7	-	9.7	-
13.3	0.0 0.0 4.52	7.6	-	**14.6**	0.0 0.0 0.0	**17.8**	0.0 0.0 0.0
13.5		**10.7**	0.0 0.0 0.0	**16.0**		**22.3**	
18.3	0.0 0.0 10.1	**11.1**		**23.7**	0.0 0.0 0.0	**31.7**	0.0 0.0 0.0
18.4		**16.2**	0.0 0.0 2.79	**24.7**		**32.2**	
21.5	-	**16.6**		**26.1**	0.0 0.0 0.0	46.4	-
22.3	-	**20.7**	0.0 0.0 0.0	**26.4**		54.9	-
27.8	-	**21.3**		**34.8**	0.0 0.0 9.03	**65.2**	0.0 0.0 0.0
28.3	-	26.9	-	**35.4**		**72.1**	
35.5	0.0 0.0 0.0	**28.7**	0.0 0.0 0.0	39.1	-	**77.6**	0.0 0.0 0.0
36.1		**29.1**		42.0	-	**82.1**	
52.4	0.0 0.0 0.0	31.8	-	**45.6**	0.0 0.0 0.0	**98.7**	0.0 0.0 0.0
52.4		**33.4**	0.0 0.0 3.99	**46.4**		**100.1**	
61.3	-	**34.7**		50.1	-	107.4	-
62.0	-	37.5	-	54.5	-	133.9	-

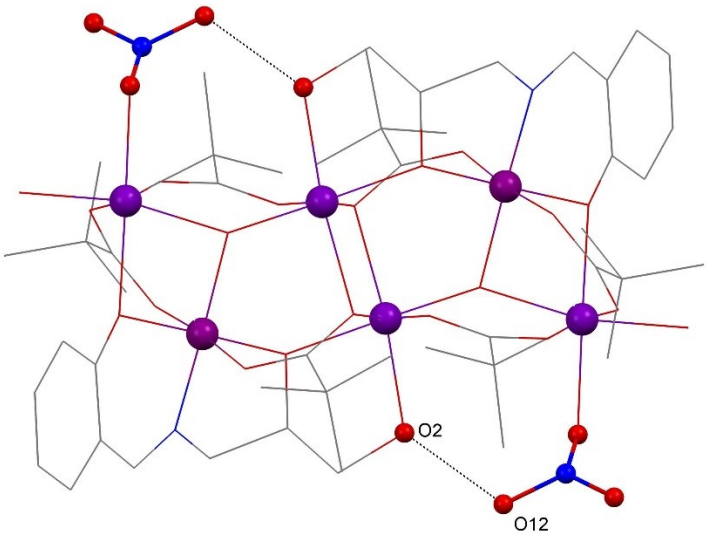

Figure SI1. Ball & stick/ wireframe molecular representation of complex **1** in crystal structure showing the intra-molecular H -interaction pattern. H atoms have been removed for sake of visualization clarity. Violet: Co(II); Purple: Co(III); Red: O; Blue: N; Grey: C.

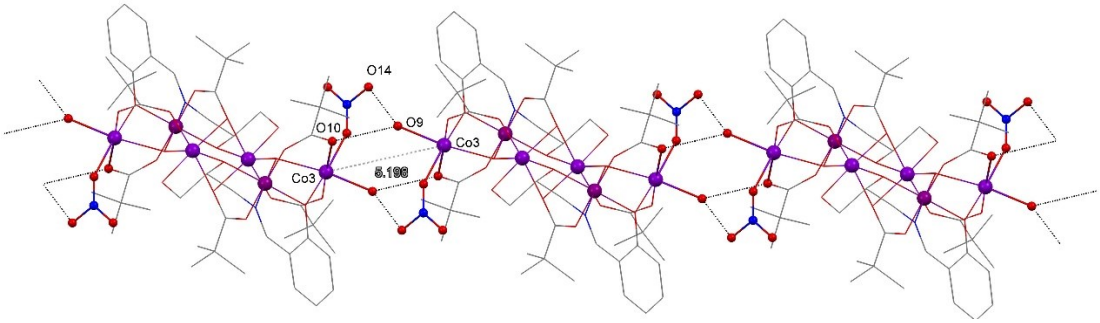

Figure SI2. Ball & stick/ wireframe molecular representation of complex **1** showing the inter-molecular H- interaction network in the crystal structure as well as the closest Co…Co inter-molecular distance in Å. H atoms have been removed for sake of visualization clarity. Violet: Co(II); Purple: Co(III); Red: O; Blue: N; Grey: C.

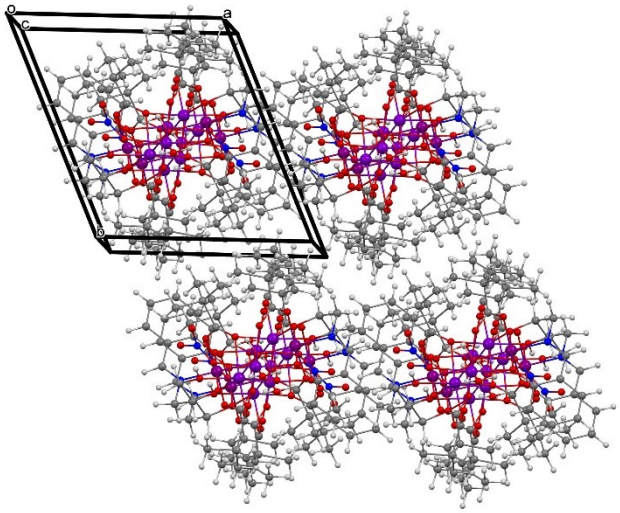

Figure SI3. Ball & stick molecular representation of complex **1** crystal packing along *c*-axis. H atoms have been removed for sake of visualization clarity. Violet: Co(II); Purple: Co(III); Red: O; Blue: N; Grey: C.

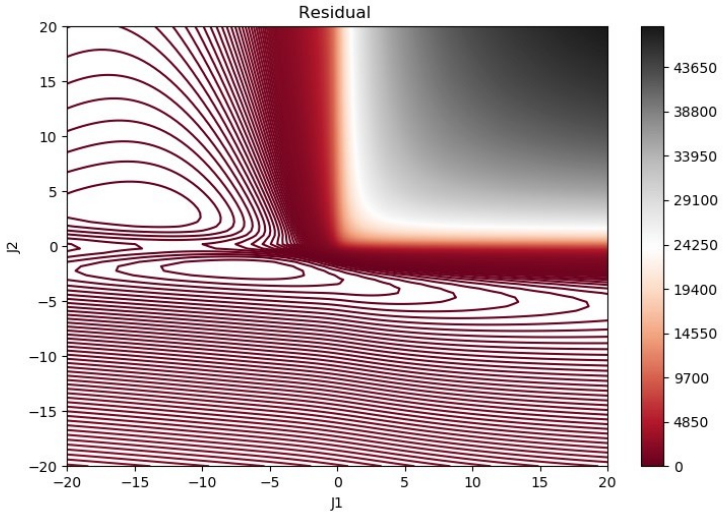

Figure SI4. χT vs T data fitting residuals contour plot showing the two minima corresponding to two different best fitting parameters sets.

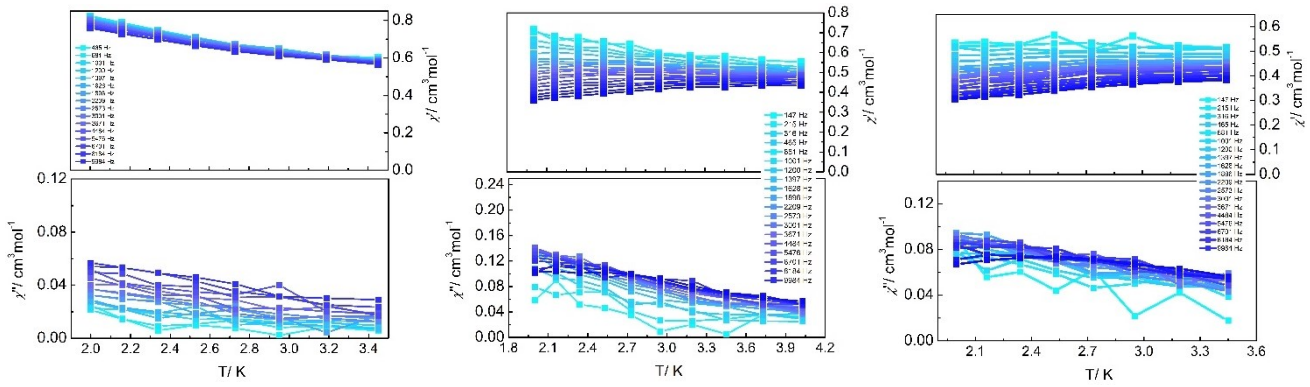

Figure SI5. AC magnetic susceptibility *vs* temperature data of complex **1** at external static fields of: 0 Oe (left), 1500 Oe (middle) and 3000 Oe (right) at driving frequencies in the range 0-10000 Hz. Full symbols: experimental data; Full lines are only for eyes guideline.

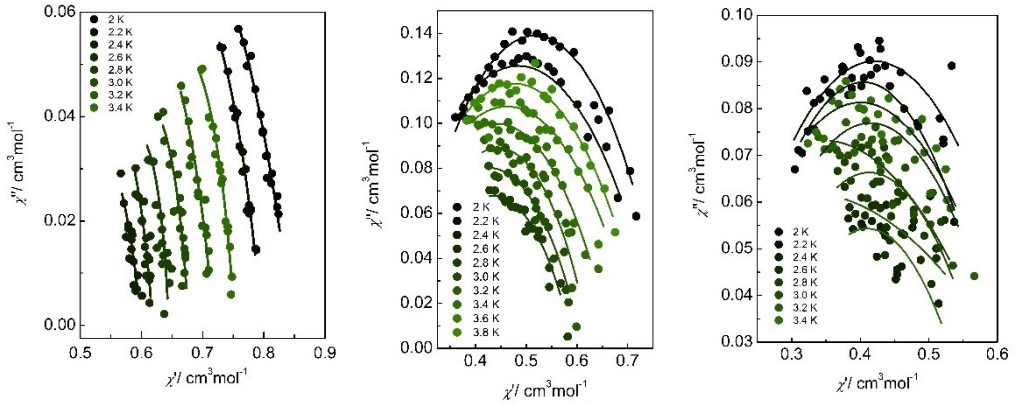

Figure SI6. AC magnetic susceptibility data Cole-Cole plots of complex **1** at external static fields of: 0 Oe (left), 1500 Oe (middle) and 3000 Oe (right) in the range 2 - 4 K. Full symbols: experimental data; Full lines: simulation with best fitting parameters according to a generalized Debye model for one relaxation process.

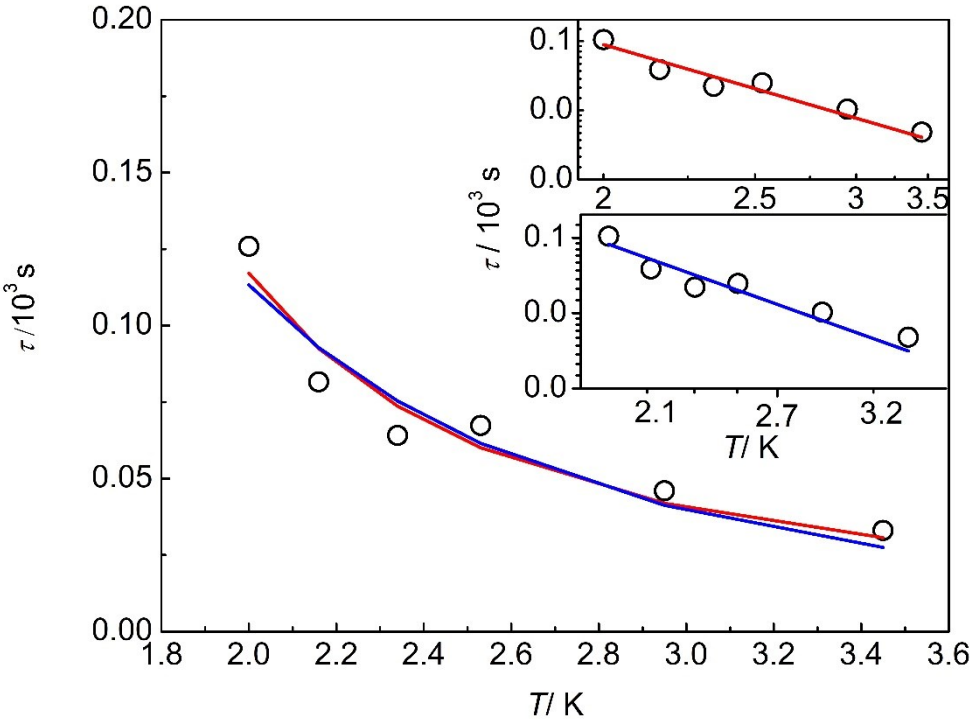

Figure SI7. Complex **1** characteristic magnetization relaxation time temperature dependence at 3000 Oe. Open circles: experimental data; full lines simulated: Orbach (blue); Raman (red). Inset: ln τ vs T^{-1} scales (top); ln τ vs ln T (bottom).

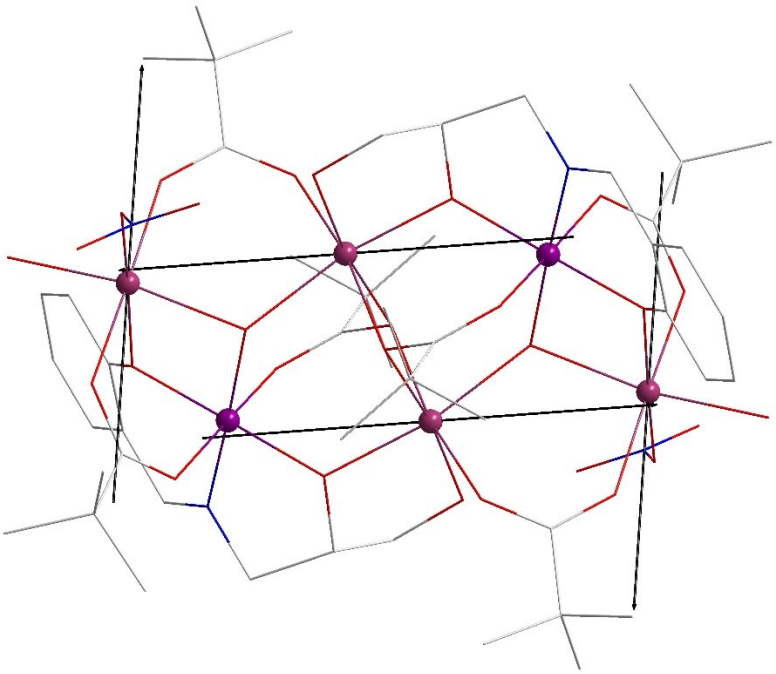

Figure SI8. Complex **1** *ab-initio* calculated main magnetic axis orientation at local Co(II) sites (black).

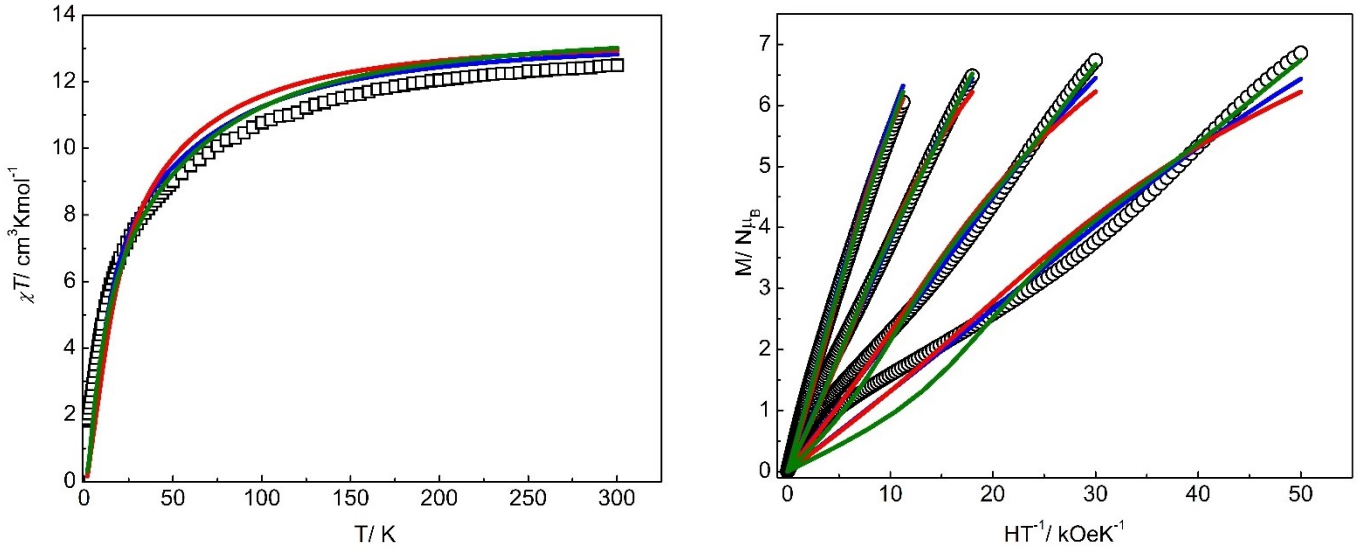

Figure SI9. Left **:** χT vs T plot measured at 1 kOe external magnetic field of complex **1**. Right: Reduced magnetization plot. Open symbols: experimental data; full line: simulation with best fitting parameters with POLY_ANISO; J_1 and $J_2 < 0$ (green), $J_1 < 0$ and $J_2 > 0$ (blue) and $J_1 > 0$ and $J_2 < 0$ (red).

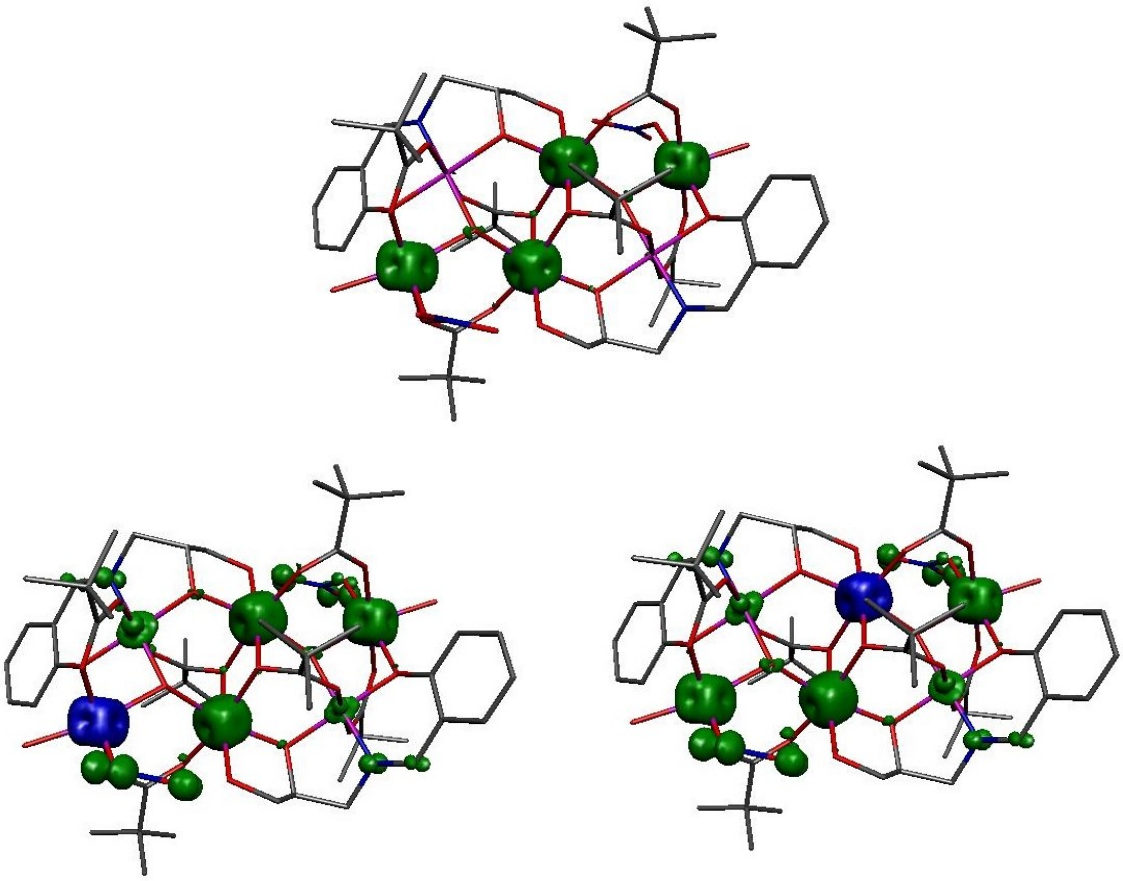

Figure SI10. Spin density iso-surfaces (0.03 a. u.), as arising from BS calculations of complex **1** (see details in text). Top: HS state; Bottom: BS states (left, BS1; right BS2) converged after sequentially flipping both symmetries distinct Co(II) sites.

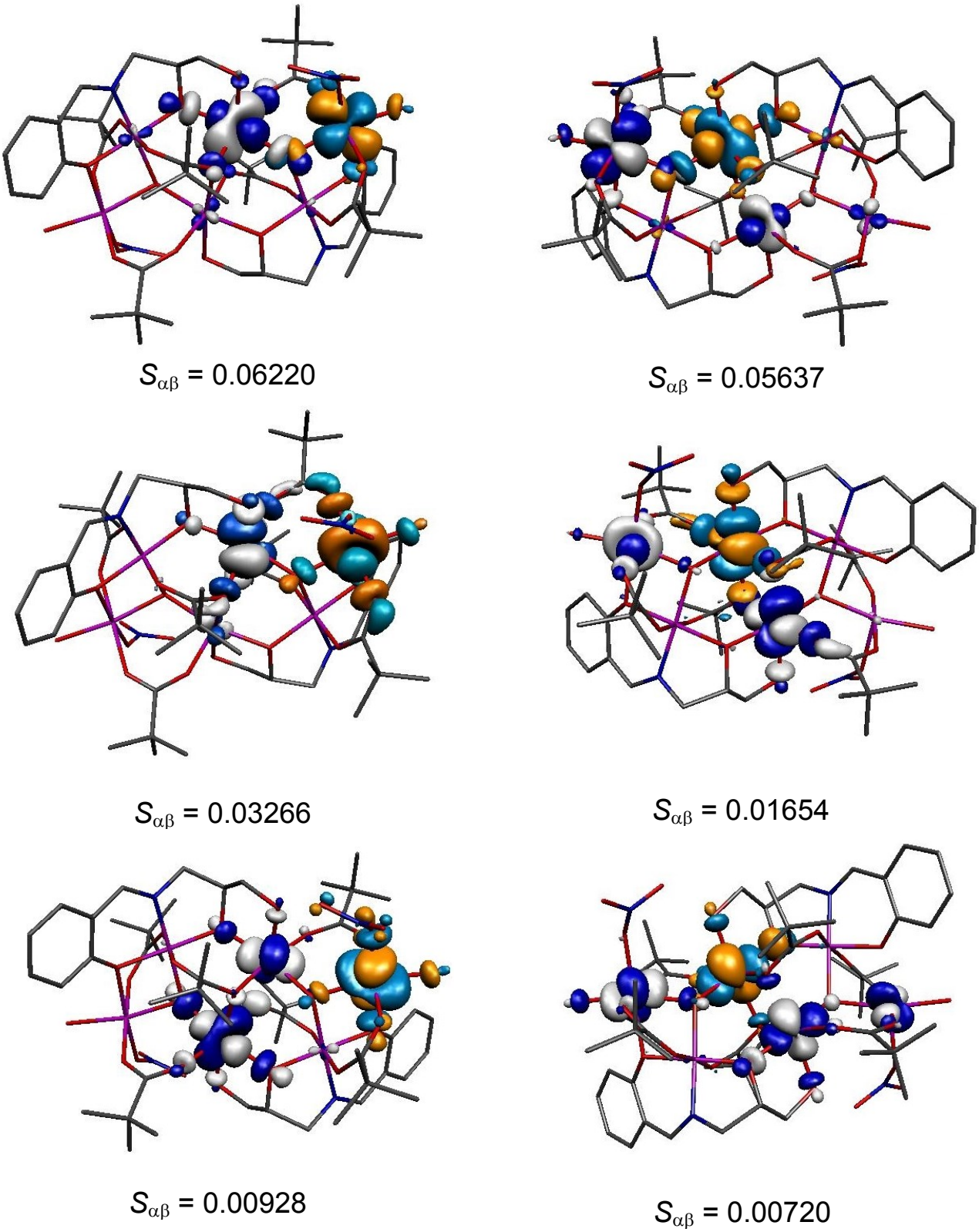

Figure SI11. Magnetic orbitals overlap ($S_{\alpha\beta}$) as arising from a COT transformation. Iso-surfaces (0.03 a. u.), as arising from BS calculations of complex **1** (see details in text; left, BS1; right BS2).