

Electronic Supplementary Information

Field-Induced Single Molecule Magnet Behavior In a Dinuclear Cobalt(II) Complex: A Combined Experimental And Theoretical Study

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Hirshfeld Surface Analysis

Hirshfeld surfaces¹⁻² and the associated two-dimensional (2D) fingerprint³⁻⁵ plots were calculated using Crystal Explorer,⁶ with bond lengths to hydrogen atoms set to standard values.⁷ For each point on the Hirshfeldisurface, two distances, d_e (the distance from the point to the nearest nucleus external to the surface) and d_i (the distance to the nearest nucleus internal to the surface), are defined. The normalized contact distance (d_{norm}) based on d_e and d_i is given by:

$$d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vdw}} + \frac{(d_e - r_e^{vdw})}{r_e^{vdw}}$$

where r_i^{vdw} and r_e^{vdw} are the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending if intermolecular contacts are shorter or longer than the van der Waals separations. The parameter d_{norm} displays a surface with a red–white–blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and

set of spherical atomic electron densities, the Hirshfeld surface is unique⁸ and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

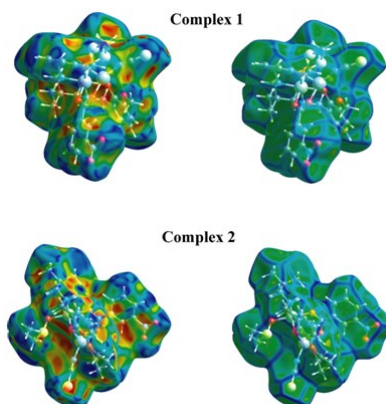


Figure S1. Hirshfeld surfaces mapped over shape index (left) and curvedness (right).

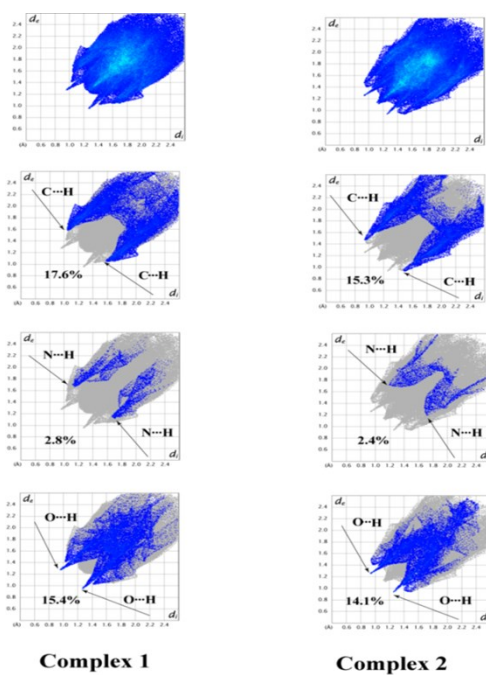


Figure S2. Fingerprint plot: Full (top), resolved into H...C/C...H (second from the top), H...N/N...H (second from the bottom) and H...O/O...H (bottom) contacts contributed to the total Hirshfeld Surface area of complexes **1** and **2**.

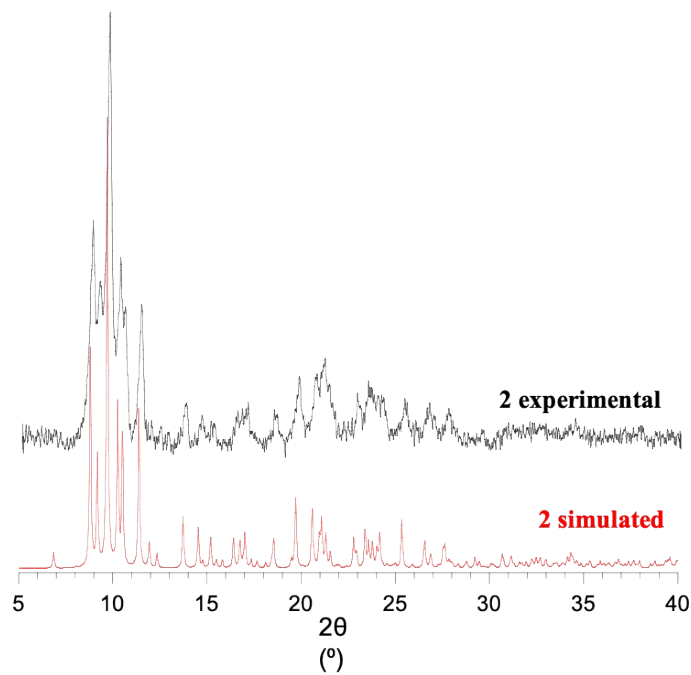


Figure S3. Experimental and simulated powder XRD patterns of complex 2 confirming the purity of bulk material.

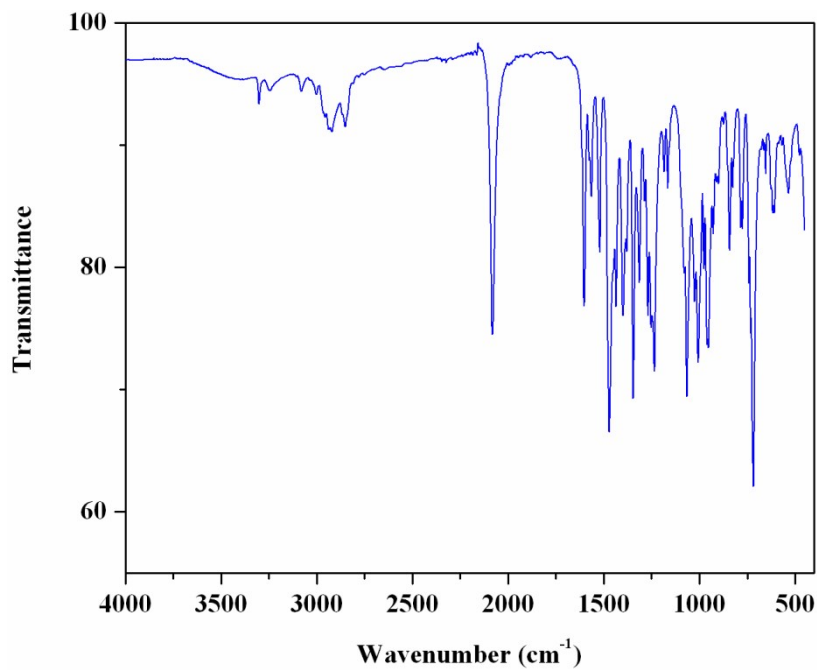


Figure S4. IR spectrum of complex 1.

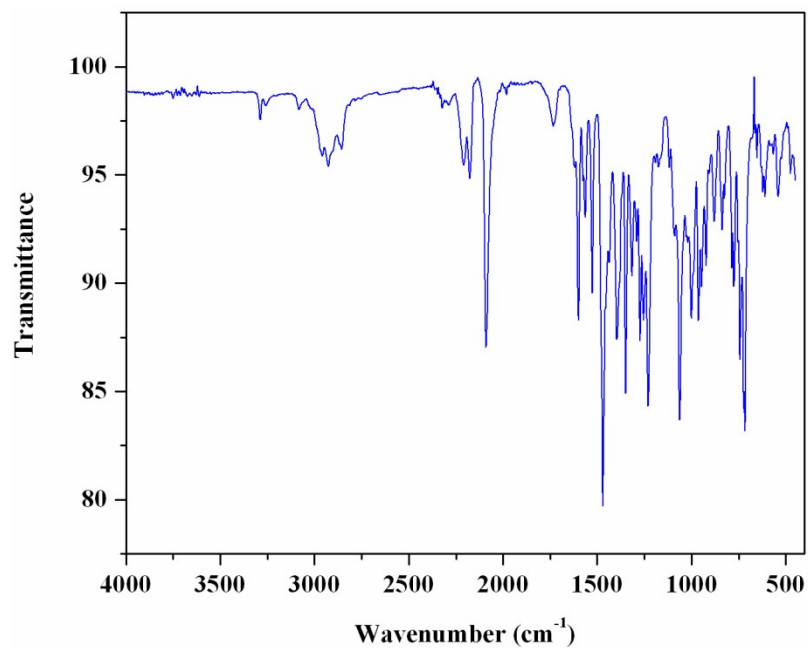


Figure S5. IR spectrum of complex 2.

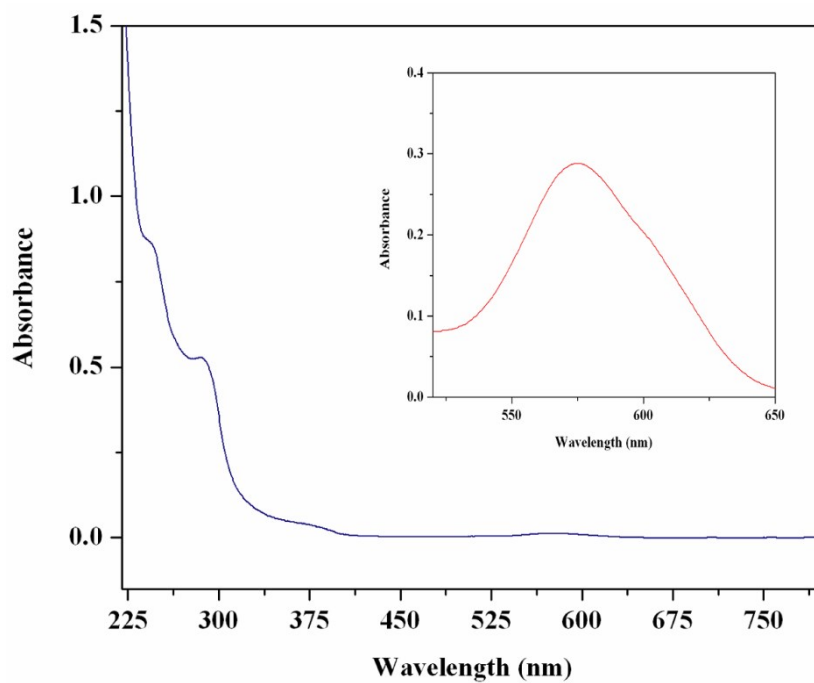


Figure S6. Electronic spectrum of complex 1. Inset shows a zoom of the 520-650 nm range.

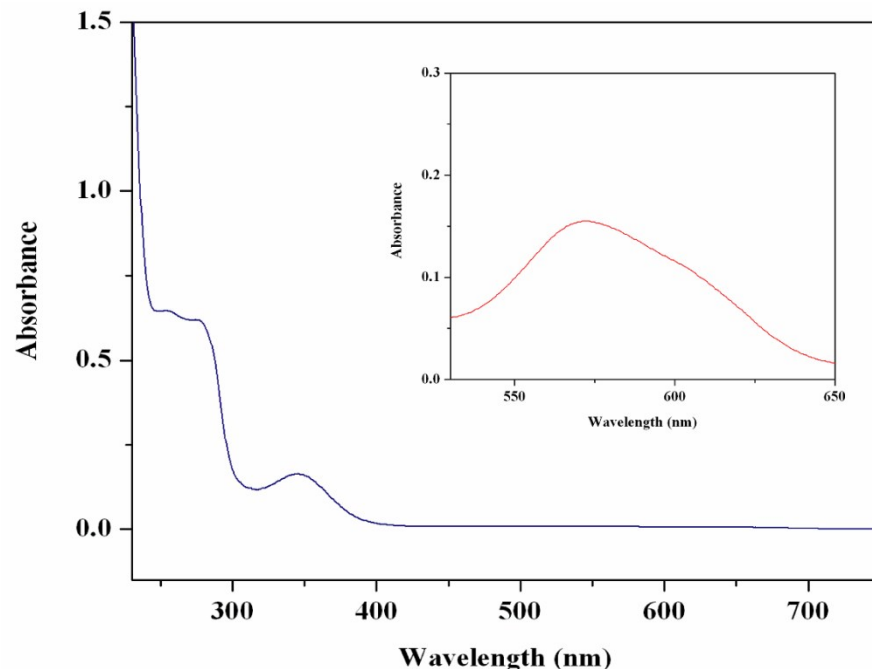


Figure S7. Electronic spectrum of complex **2**. Inset shows a zoom of the 520-650 nm.

Table S1. Selected bond angles ($^{\circ}$) in complexes **1** and **2**.

Atoms	1	2	Atoms	1	2
O1-Co1-O2	80.39(9)	80.92(3)	O1-Co2-O2	83.30(9)	84.39(3)
O1-Co1-O5	90.27(8)	93.88(4)	O1-Co2-O3	71.88(8)	73.20(2)
O1-Co1-O9	92.90(8)	87.10(2)	O1-Co2-O4	156.05(10)	153.40(2)
O1-Co1-N1	91.83(11)	172.80(2)	O1-Co2-O6	96.73(9)	97.90(2)
O1-Co1-N2	172.23(9)	92.4(2)	O1-Co2-N3	111.62(15)	113.40(3)
O2-Co1-O5	92.58(9)	87.38(3)	O2-Co2-O3	154.38(9)	156.10(2)
O2-Co1-O9	92.11(9)	90.20(2)	O2-Co2-O4	73.10(10)	70.10(2)
O2-Co1-N1	171.87(11)	91.90(2)	O2-Co2-O6	99.26(9)	94.50(2)
O2-Co1-N2	91.93(9)	173.10(2)	O2-Co2-N3	116.08(14)	108.70(3)
O5-Co1-O9	174.72(9)	177.20(2)	O3-Co2-O4	130.81(10)	130.60(3)
O5-Co1-N1	85.07(10)	86.53(4)	O3-Co2-O6	77.98(9)	81.00(2)
O5-Co1-N2	88.92(9)	91.50(4)	O3-Co2-N3	80.05(14)	88.00(3)
O9-Co1-N1	90.60(10)	92.10(2)	O4-Co2-O6	83.20(10)	77.70(2)
O9-Co1-N2	88.50(9)	91.00(2)	O4-Co2-N3	83.30(15)	82.60(3)
N1-Co1-N2	95.80(11)	94.80(2)	O6-Co2-N3	136.22(15)	142.20(3)

SHAPE analysis of the coordination geometry around Co1 and Co2 in both complexes

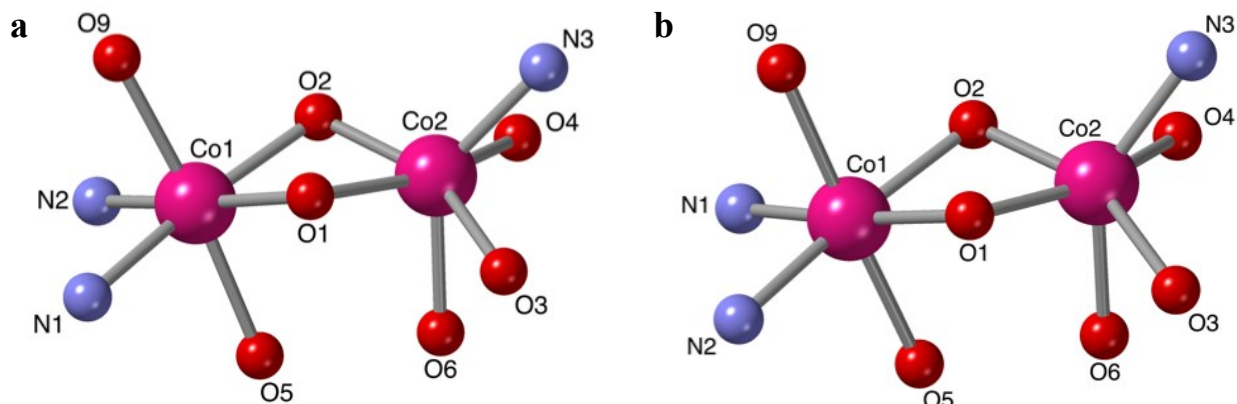


Figure S8. Coordination geometry of both Co atoms in complexes **1** (a) and **2** (b)

Table S2. SHAPE⁹ values for the five possible coordination geometries for coordination number six¹⁰ in both Co centres in [(dmsO)Co^{II}L¹(μ -(*m*-NO₂)C₆H₄COO)Co^{II}(NCS)] (**1**) and [(dmsO)Co^{II}L²(μ -(*m*-NO₂)C₆H₄COO)Co^{II}(NCS)] (**2**).

Compound		1		2	
Geometry	symmetry	Co1	Co2	Co1	Co2
HP-6	D6h	31.981	29.700	31.191	30.120
PPY-6	C5v	26.975	10.730	27.142	12.980
OC-6	Oh	0.404	9.725	0.275	9.117
TPR-6	D3h	13.946	7.097	14.744	7.839
JPPY-6	C5v	30.909	13.401	31.048	15.308

HP-6 = Hexagon, PPY-6 = Pentagonal pyramid, OC-6 = Octahedron, TPR-6 = Trigonal prism, JPPY-6 = Johnson pentagonal pyramid J2. Minima values are indicated in bold.

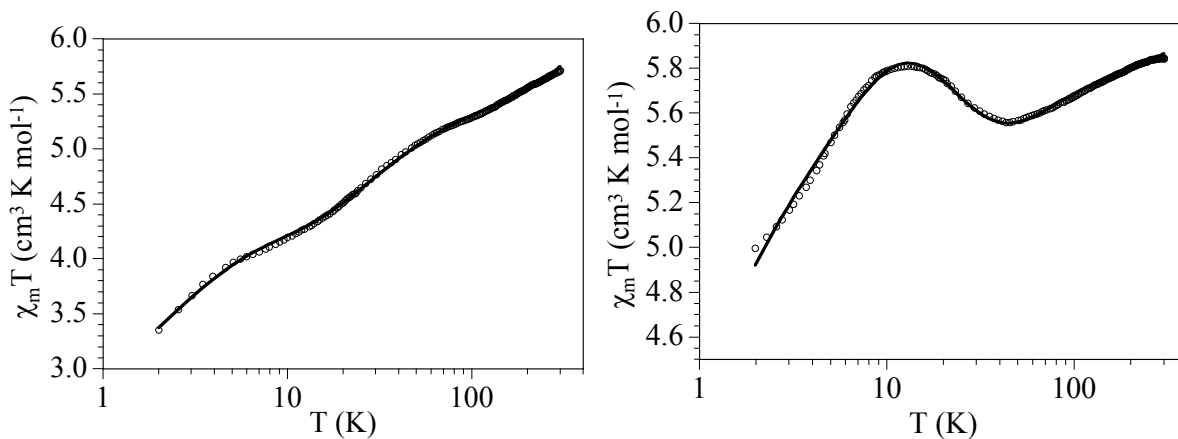


Figure S9. Thermal variation (logarithmic scale) of the $\chi_m T$ product for complexes **1** (left) and **2** (right).

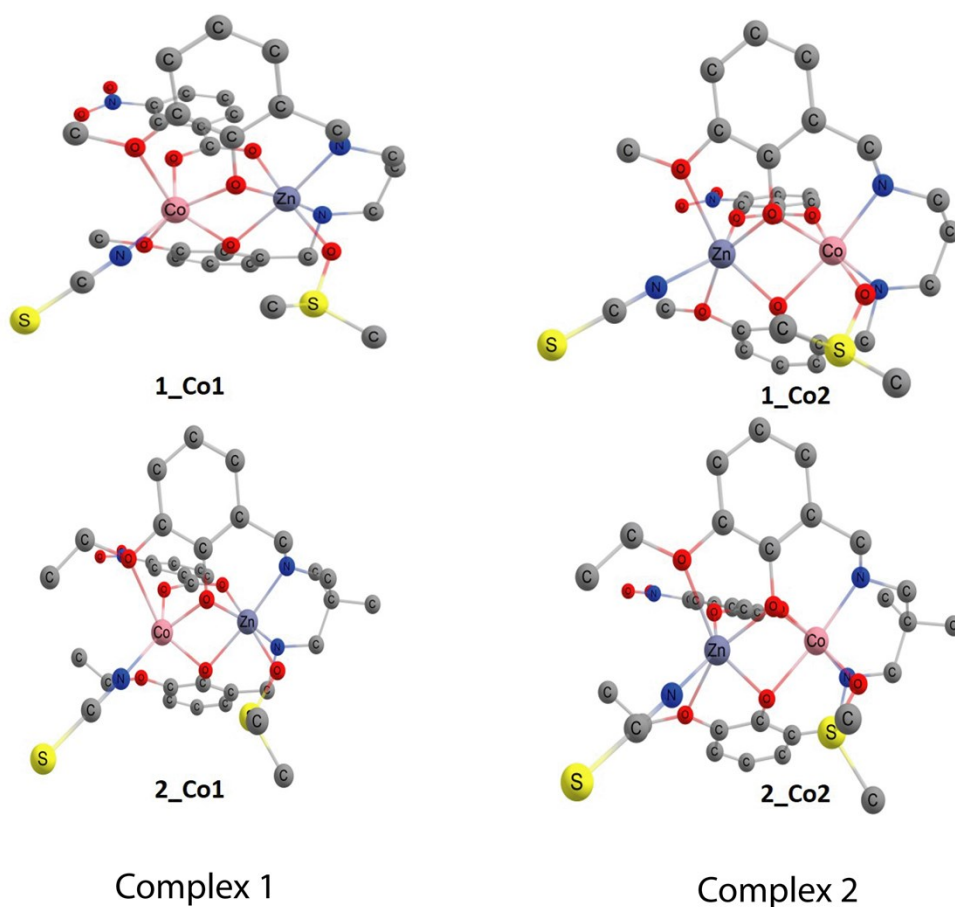


Figure S10. Pictorial view of diamagnetic substitution method applied to calculate the ZFS of two cobalt centers in complexes **1** and **2**.

References

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