Supporting Information

A Trinuclear Nickel(II) Schiff Base Complex with Phenoxido- and Acetato-Bridges: Combined Experimental and Theoretical Magneto-structural Correlation

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Table S1. Hydrogen bond in complex **1** (distances in Å and angles in degrees).

D-H···A	D-H	H···A	D···A	< (D-H-A)
O1M-H1M···O1A$^{\#}$	0.76(2)	2.01(2)	2.7575(17)	173(2)

Symmetry transformations used to generate equivalent atoms:

= -x + 1, y, -z + ½

Table S2. Selected optimized structural parameters of complex **1** in HS and BS spin states, obtained with various DFT functionals.

Functional	Spin state	Ni1–O1	Ni1-O1A	Ni1-O2	Ni2–O1/ Ni3-O1	Ni2–O2A/ Ni3–O2A	Ni2-O1M/ Ni3-O1M	Ni2-N/ Ni3-N	Ni2-N1/ Ni3-N1	Ni2-N2/ Ni3-N2	Ni3–O1–Ni 1	Ni2–O1–Ni 1
B3LYP	HS ααα	2.06	2.03	2.13	2.08	2.08	2.18	2.01	2.02	2.12	116.81	116.81
	BS ααβ	2.06	2.03	2.13	2.08	2.08	2.18	2.01	2.02	2.12	116.81	116.96
	BS αβα	2.06	2.03	2.12	2.08	2.08	2.18	2.01	2.02	2.12	116.96	116.97
B3LYP*	HS ααα	2.07	2.05	2.14	2.10	2.11	2.20	2.01	2.04	2.13	118.68	118.50
	BS ααβ	2.07	2.05	2.14	2.10	2.11	2.20	2.01	2.04	2.13	118.48	118.90
	BS αβα	2.07	2.05	2.14	2.10	2.11	2.20	2.01	2.04	2.13	118.85	118.78
TPSSh	HS ααα	2.04	2.01	2.10	2.06	2.07	2.15	1.98	2.01	2.09	119.03	118.92
	BS ααβ	2.04	2.01	2.10	2.06	2.07	2.15	1.98	2.01	2.09	118.64	118.98
	BS αβα	2.04	2.01	2.10	2.06	2.07	2.15	1.98	2.01	2.09	119.03	119.15
Experimental data XRD		2.0134(11)	2.0212(11)	2.1166(11)	2.0472(11)	2.0465(12)	2.1874(12)	2.0236(16)	2.0195(15)	2.0666(15)	117.87(5)	117.87(5)

Table S3. Total energies (*E*, a.u.), relative energies (ΔE, kcal mol^{-1}) and expectation values of the spin-squared (<S^2>) operator for the high-spin and broken symmetry (BS) states of the complex **1** calculated by the DFT method with different functionals.

Functional	Spin state	*S*	*E*, a.u.	Δ*E*, kcal/mol	< S^2 >
B3LYP	HS (ααα)	3/2	-7799.001444	0.049	12.011
	BS (ααβ)	1/2	-7799.001483	0.024	4.008
	BS (αβα)	1/2	-7799.001522	0	4.006
B3LYP*	HS (ααα)	3/2	-7771.134572	0.196	12.011
	BS (ααβ)	1/2	-7771.13473	0.097	4.006
	BS (αβα)	1/2	-7771.134885	0	4.001
TPSSh	HS (ααα)	3/2	-7799.013977	0.206	12.011
	BS (ααβ)	1/2	-7799.01414	0.104	4.006
	BS (αβα)	1/2	-7799.014306	0	4.001

Table S4. Mulliken spin populations (ρ) and total charges (q) on atoms of the exchange fragment (B3LYP/6-311G(d,p)) in high (HS) and low spin states (BS).

Atom	HS	BS (αβα)	BS (ααβ)
	ρ/q	ρ/q	ρ/q
Ni1	1.766/1.454	-1.763/1.453	1.765/1.454
Ni2	1.739/1.469	1.738/1.468	-1.738/1.468
Ni3	1.739/1.469	1.738/1.468	1.739/1.469
O27	0.071/-0.788	-0.003/-0.788	0.071/-0.788
O4	0.071/-0.786	-0.003/-0.788	0.003/-0.788
N34	0.065/-0.545	0.065/-0.545	0.065/-0.545
N10	0.065/-0.545	0.065/-0.545	-0.065/-0.545

X-ray powder analysis

The X-ray powder diffractogram was collected for a polycrystalline sample of compound **1** using a 0.5 mm glass capillary that was mounted and aligned on an Empyrean PAN analytical powder diffractometer, using CuKα (λ = 1.54177 Å). A total of 3 scans were collected at room temperature in the 2θ range 5-40°.

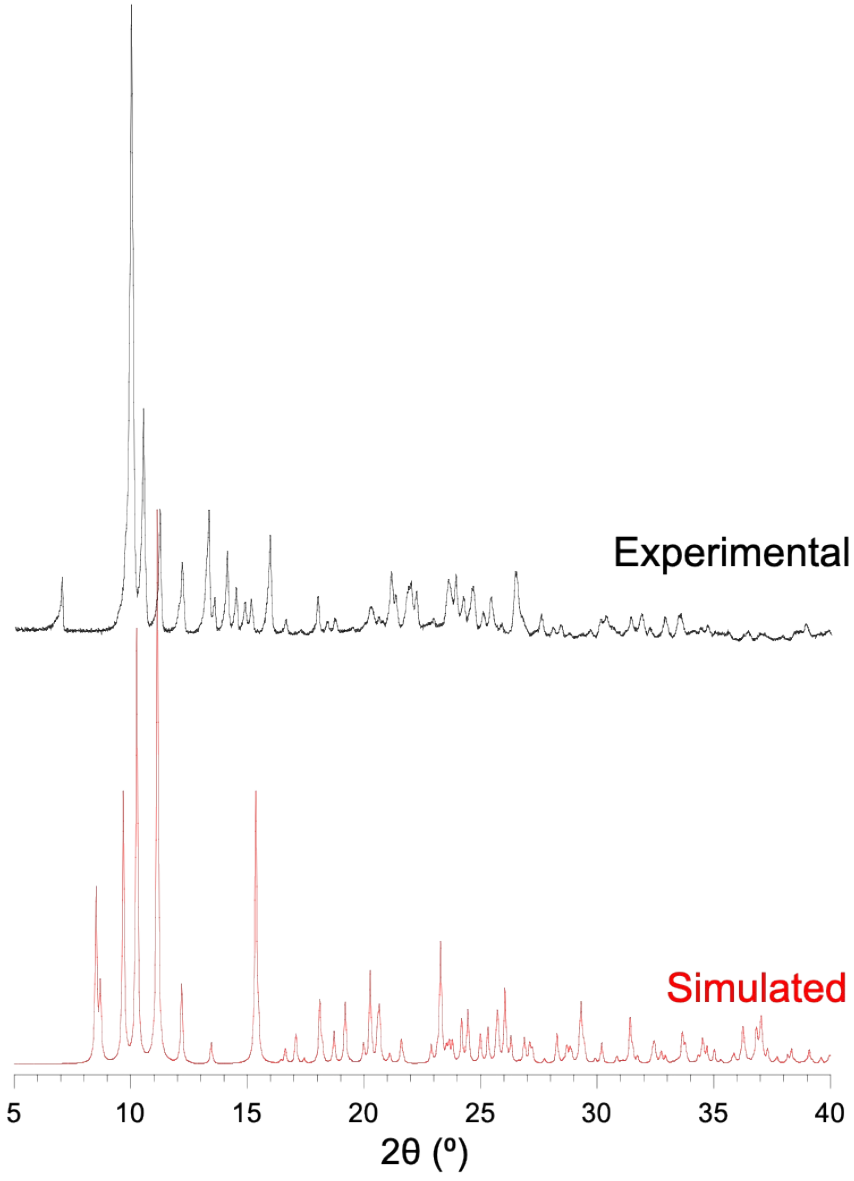

Figure S1. X-ray powder diffractogram for complex **1** and the simulated one from the cif file.

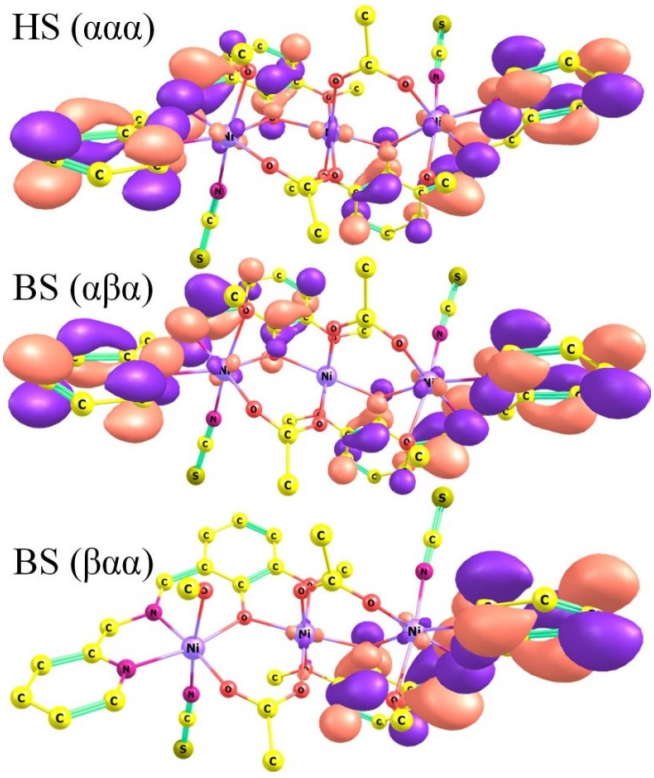

Fig. S2. Shape of the localized magnetically active SOMOs of the complex **1** (hydrogen atoms are removed for clarity, contour value is 0.03 e·Å^{-3}) that are occupied by three "parallel" α-spins for the HS state and "opposite" α/β-spins for the BS state.