SUPPORTING INFORMATION

Synthesis, characterization and magnetic properties of halogenated tetranuclear cubane-like nickel(II) complexes

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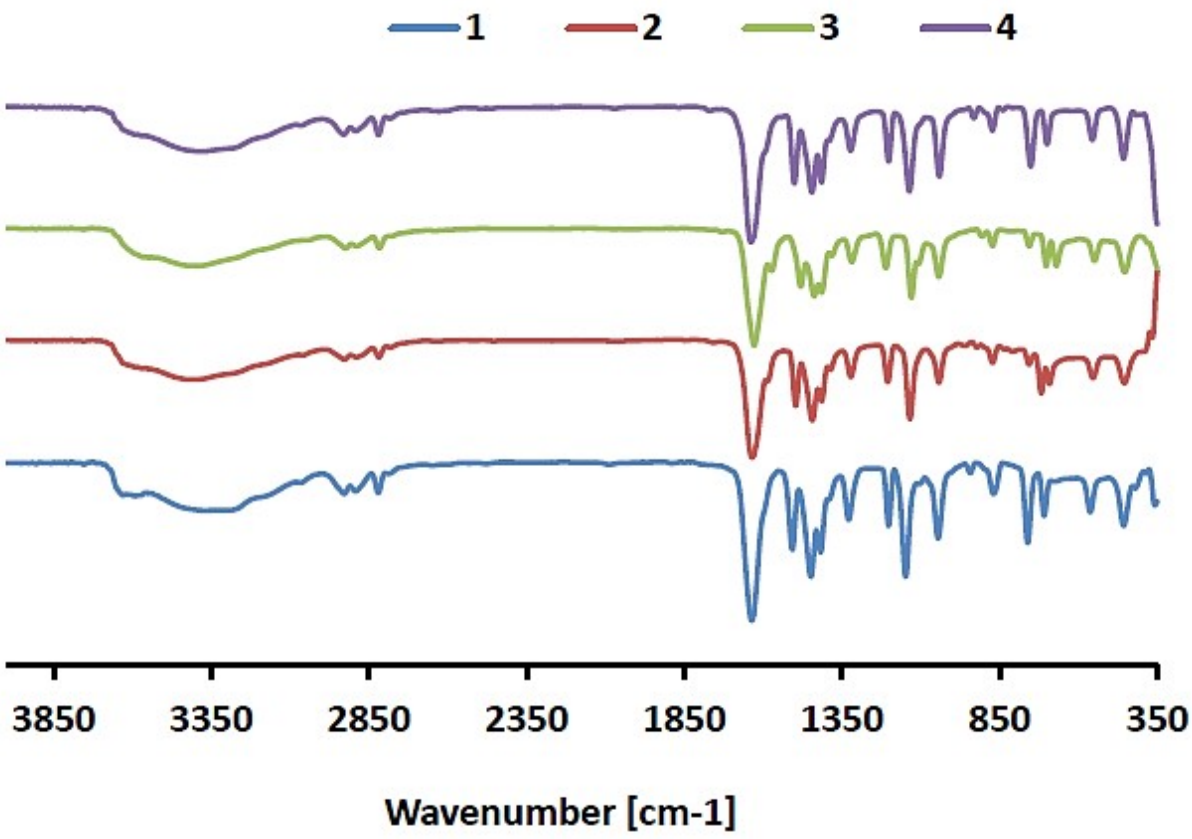

Figure S1. FT-IR spectra of **1**, **2**, **3** and **4** complexes.

Table S1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{36}H_{40}Br_4Cl_4Ni_4O_{16}$
Formula weight	1424.96
Temperature (K)	302(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	a = 17.1504(12)
	b = 18.4070(14)
	c = 15.3957(12)
	β = 90.952(3)
Volume ($Å^3$)	4859.6(6)
Z	4
Calculated density (Mg/m^3)	1.948
Absorption coefficient (mm^{-1})	5.099
F(000)	2816
Theta range for data collection (°)	2.848 to 24.999
Index ranges	-20≤ h ≤20
	-21≤ k ≤21
	-18≤ l ≤18
Reflections collected	93557
Independent reflections	8553 [$R_{(int)}$ = 0.1217]
Data Completeness (%)	99.9
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8553 / 10 / 598
Goodness-of-fit on F^2	1.093
Final R indices [I>2σ (I)]	R_1 = 0.0628
	wR_2 = 0.1064
R indices (all data)	R_1 = 0.1160
	wR_2 = 0.1339
Largest diff. peak and hole ($e.Å^{-3}$)	0.810 and -0.956
CCDC number	2311186

Table S2. Selected bond lengths (Å) and angles (°) for **4**.

Ni(1)-O(1)	1.991(5)	O(10)-Ni(1)-O(9)	83.4(2)
Ni(1)-O(10)	2.030(5)	O(10)-Ni(1)-O(11)	82.2(2)
Ni(1)-O(2)	2.041(6)	O(9)-Ni(1)-O(11)	82.7(2)
Ni(1)-O(9)	2.049(5)	O(11)-Ni(2)-O(12)	83.7(2)
Ni(1)-O(11)	2.059(5)	O(11)-Ni(2)-O(10)	82.3(2)
Ni(1)-O(13)	2.113(6)	O(12)-Ni(2)-O(10)	82.9(2)
Ni(2)-O(3)	2.013(6)	O(9)-Ni(3)-O(11)	83.3(2)
Ni(2)-O(11)	2.031(5)	O(9)-Ni(3)-O(12)	81.1(2)
Ni(2)-O(12)	2.037(5)	O(11)-Ni(3)-O(12)	82.15(19)
Ni(2)-O(4)	2.043(6)	O(10)-Ni(4)-O(12)	83.3(2)
Ni(2)-O(10)	2.052(5)	O(12)-Ni(4)-O(9)	81.5(2)
Ni(2)-O(15)	2.153(6)	O(10)-Ni(4)-O(9)	83.3(2)
Ni(3)-O(5)	1.998(6)	Ni(3)-O(9)-Ni(1)	97.0(2)
Ni(3)-O(9)	2.029(5)	Ni(3)-O(9)-Ni(4)	99.0(2)
Ni(3)-O(6)	2.033(6)	Ni(4)-O(9)-Ni(1)	95.5(2)
Ni(3)-O(11)	2.057(5)	Ni(1)-O(10)-Ni(4)	96.5(2)
Ni(3)-O(12)	2.073(5)	Ni(1)-O(10)-Ni(2)	97.6(2)
Ni(3)-O(14)	2.127(6)	Ni(4)-O(10)-Ni(2)	96.2(2)
Ni(4)-O(7)	2.026(6)	Ni(2)-O(11)-Ni(3)	96.9(2)
Ni(4)-O(8)	2.033(6)	Ni(2)-O(11)-Ni(1)	97.4(2)
Ni(4)-O(10)	2.035(5)	Ni(3)-O(11)-Ni(1)	95.8(2)
Ni(4)-O(12)	2.037(5)	Ni(2)-O(12)-Ni(4)	96.6(2)
Ni(4)-O(9)	2.048(5)	Ni(2)-O(12)-Ni(3)	96.2(2)
Ni(4)-O(16)	2.087(7)	Ni(4)-O(12)-Ni(3)	97.9(2)
Ni(1)-Ni(2)	3.0724(16)		
Ni(1)-Ni(3)	3.0531(15)		
Ni(1)-Ni(4)	3.0332(15)		
Ni(2)-Ni(3)	3.0588(15)		
Ni(2)-Ni(4)	3.0407(15)		
Ni(3)-Ni(4)	3.1001(15)		

Table S3. Non-classical hydrogen bonds and other intermolecular interactions with distances shorter than the sum of van der Waals radii for **4**

D—H...A	**D—H**	**H...A**	**D...A**	**D—H...A**	**Symmetry codes**
C36—H36A…Cl2	0.96	2.69	3.543(13)	149	2-x, ½+y, ½-z
C17—H17…Br1	0.93	3.07	3.458(9)	107	2-x, 1-y, -z
C21—H21…H29B—C29	0.93, 0.96	2.30	3.585(13)	157, 110	1-x, -y, 1-z
C21—H21…H29A—C29	0.93, 0.96	2.51	3.585(13)	125, 96	1-x, -y, 1-z
C26—H26…H34A—C34	0.93, 0.96	2.59	3.645(13)	129, 94	1-x, -y, 1-z
C26—H26…H34B—C34	0.93, 0.96	2.51	3.645(13)	165, 99	1-x, -y, 1-z

Table S4. Comparison of experimental and theoretical structures for compound **4**.

	DFT	Experimental
Ni1-Ni2	3.110	3.072
Ni1-Ni3	3.039	3.053
Ni1-Ni4	3.041	3.033
Ni2-Ni3	3.042	3.059
Ni2-Ni4	3.039	3.041
Ni3-Ni4	3.108	3.100
Ni1-O9	2.061	2.049
Ni1-O10	2.048	2.030
Ni1-O11	2.053	2.058
Ni2-O10	2.053	2.052
Ni2-O11	2.049	2.031
Ni2-O12	2.059	2.037
Ni3-O9	2.047	2.029
Ni3-O11	2.059	2.058
Ni3-O12	2.054	2.073
Ni4-O9	2.056	2.048
Ni4-O10	2.058	2.034
Ni4-O12	2.047	2.038
Ni1-O10-Ni2	98.6	97.65
Ni1-O11-Ni2	98.6	97.41
Ni1-O9-Ni3	95.4	96.95
Ni1-O11-Ni3	95.3	95.76
Ni1-O9-Ni4	95.3	95.52
Ni1-O10-Ni4	95.6	96.53
Ni2-O11-Ni3	95.5	96.87
Ni2-O12-Ni3	95.4	96.16
Ni2-O10-Ni4	95.3	96.18
Ni2-O12-Ni4	95.5	96.51
Ni3-O9-Ni4	98.5	98.97
Ni3-O12-Ni4	98.5	97.87
Ni1-Ni2-Ni3-Ni4	69.3	69.56
O9-O10-O11-O12	67.7	68.96

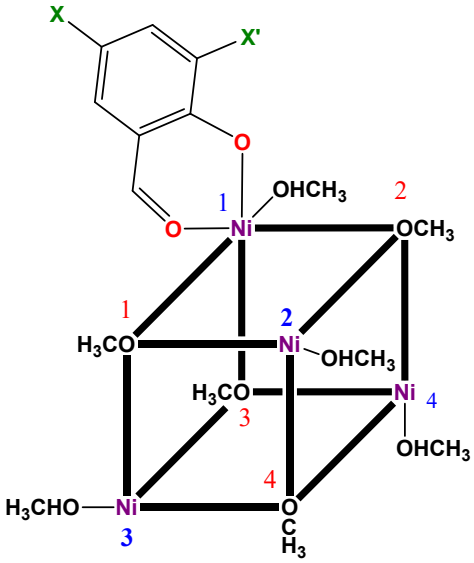

Figure S2. Atom labeling for tables in Supporting Information

Table S5. Calculated magnetic coupling constants J for compounds **1-3**.

	Compound **1**	
	Distance (Å)	J calc.(cm^{-1})
Ni1-Ni2	3.115	J_1 = 6.58
Ni1-Ni3	3.041	J_2 = 13.08
Ni1-Ni4	3.041	J_3 = 13.46
Ni2-Ni3	3.041	J_4 = 13.47
Ni2-Ni4	3.041	J_5 = 13.15
Ni3-Ni4	3.115	J_6 = 6.73
	Compound **2**	
	Distance (Å)	J calc.(cm^{-1})
Ni1-Ni2	3.114	J_1 = 6.87
Ni1-Ni3	3.041	J_2 = 12.92
Ni1-Ni4	3.041	J_3 = 13.28
Ni2-Ni3	3.041	J_4 = 13.18
Ni2-Ni4	3.041	J_5 = 12.95
Ni3-Ni4	3.114	J_6 = 6.88
	Compound **3**	
	Distance (Å)	J calc.(cm^{-1})
Ni1-Ni2	3.116	J_1 = 7.74
Ni1-Ni3	3.040	J_2 = 13.10
Ni1-Ni4	3.040	J_3 = -6439.48
Ni2-Ni3	3.040	J_4 = 13.46
Ni2-Ni4	3.040	J_5 = 13.20
Ni3-Ni4	3.116	J_6 = 7.54

Table S6. Calculated magnetic coupling constants *J* for compound **4** considering both optimized and experimental structures.

Compound **4**				
	DFT Calculated		Experimental Values	
	Distance (Å)	*J* DFT.(cm^{-1})	Distance (Å)	*J* calc.(cm^{-1})
Ni1-Ni2	3.110	J_1 = 7.45	3.072	J_1 = 12.06
Ni1-Ni3	3.039	J_2 = 12.88	3.053	J_2 = 12.56
Ni1-Ni4	3.041	J_3 = 12.95	3.033	J_3 = 14.01
Ni2-Ni3	3.042	J_4 = 12.86	3.059	J_4 = 12.30
Ni2-Ni4	3.039	J_5 = 12.99	3.041	J_5 = 13.58
Ni3-Ni4	3.108	J_6 = 7.74	3.100	J_6 = 8.53

Table S7. Mulliken spin densities computed for the high spin configuration of the [Ni_2] dimer model of compound **1**. See Figure S1 for labeling of atoms.

Atom Label[a]	Spin Density	Atom Label[a]	Spin Density
		J_1	
Ni(1)	1.725	Ni(2)	1.725
O_{CH3O-}(1)	0.105	O_{CH3O-}(2)	0.105
O_{CH3O-}(3)	0.052	O_{CH3O-}(4)	0.052
O_{CH3OH}(1)	0.032	O_{CH3OH}(2)	0.032
$O_{aldehyde}$(1)	0.034	$O_{phenoxy}$(1)	0.037
$O_{aldehyde}$(2)	0.034	$O_{phenoxy}$(2)	0.037
		J_2	
Ni(1)	1.724	Ni(3)	1.724
O_{CH3O-}(1)	0.106	O_{CH3O-}(2)	0.052
O_{CH3O-}(3)	0.103	O_{CH3O-}(4)	0.054
O_{CH3OH}(1)	0.032	O_{CH3OH}(3)	0.032
$O_{aldehyde}$(1)	0.034	$O_{phenoxy}$(1)	0.037
$O_{aldehyde}$(3)	0.034	$O_{phenoxy}$(3)	0.037
		J_3	
Ni(1)	1.724	Ni(4)	1.724
O_{CH3O-}(1)	0.054	O_{CH3O-}(2)	0.103
O_{CH3O-}(3)	0.106	O_{CH3O-}(4)	0.052
O_{CH3OH}(1)	0.032	O_{CH3OH}(4)	0.032
$O_{aldehyde}$(1)	0.034	$O_{phenoxy}$(1)	0.037
$O_{aldehyde}$(4)	0.034	$O_{phenoxy}$(4)	0.037
		J_4	
Ni(2)	1.724	Ni(3)	1.724
O_{CH3O-}(1)	0.103	O_{CH3O-}(2)	0.054
O_{CH3O-}(3)	0.052	O_{CH3O-}(4)	0.106
O_{CH3OH}(2)	0.032	O_{CH3OH}(3)	0.032
$O_{aldehyde}$(2)	0.034	$O_{phenoxy}$(2)	0.037
$O_{aldehyde}$(3)	0.034	$O_{phenoxy}$(3)	0.037
		J_5	
Ni(2)	1.724	Ni(4)	1.724
O_{CH3O-}(1)	0.052	O_{CH3O-}(2)	0.106
O_{CH3O-}(3)	0.054	O_{CH3O-}(4)	0.103

$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.037
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.037
J_6			
Ni(3)	1.725	Ni(4)	1.725
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.105	$O_{CH3O-}(4)$	0.105
$O_{CH3OH}(3)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(3)$	0.034	$O_{phenoxy}(3)$	0.037
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.037

[a]O_{CH3O-}(X) methoxy(X), O_{CH3OH}(X) methanol bonded to Ni(X), $O_{aldehyde}$(X) aldehyde oxygen bonded to Ni(X), $O_{phenoxy}$(X) phenoxy oxygen bonded to Ni(X).

Table S8. Mulliken spin densities computed for the high spin configuration of the [Ni_2] dimer models of compound **2**. See Figure S1 for labeling of atoms.

Atom Label[a]	Spin Density	Atom Label[a]	Spin Density
J_1			
Ni(1)	1.724	Ni(2)	1.724
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.052
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(2)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.036
J_2			
Ni(1)	1.724	Ni(3)	1.724
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.104	$O_{CH3O-}(4)$	0.055
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(3)$	0.034	$O_{phenoxy}(3)$	0.036
J_3			
Ni(1)	1.724	Ni(4)	1.724
$O_{CH3O-}(1)$	0.055	$O_{CH3O-}(2)$	0.104
$O_{CH3O-}(3)$	0.106	$O_{CH3O-}(4)$	0.052
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.036
J_4			
Ni(2)	1.724	Ni(3)	1.724
$O_{CH3O-}(1)$	0.104	$O_{CH3O-}(2)$	0.055
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.036
$O_{aldehyde}(3)$	0.034	$O_{phenoxy}(3)$	0.036
J_5			
Ni(2)	1.724	Ni(4)	1.724
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.055	$O_{CH3O-}(4)$	0.104

$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.036
J_6			
Ni(3)	1.724	Ni(4)	1.724
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.106	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(3)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(3)$	0.034	$O_{phenoxy}(3)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.036

[a]O_{CH3O-}(X) methoxy(X), O_{CH3OH}(X) methanol bonded to Ni(X), $O_{aldehyde}$(X) aldehyde oxygen bonded to Ni(X), $O_{phenoxy}$(X) phenoxy oxygen bonded to Ni(X).

Table S9. Mulliken spin densities computed for the high spin configuration of the [Ni_2] dimer models of compound **3**. See Figure S1 for labeling of atoms.

Atom Label[a]	Spin Density	Atom Label[a]	Spin Density
J_1			
Ni(1)	1.724	Ni(2)	1.724
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.052
$O_{CH3OH}(1)$	0.031	$O_{CH3OH}(2)$	0.031
$O_{aldehyde}(1)$	0.035	$O_{phenoxy}(1)$	0.035
$O_{aldehyde}(2)$	0.035	$O_{phenoxy}(2)$	0.035
J_2			
Ni(1)	1.723	Ni(3)	1.723
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.053
$O_{CH3O-}(3)$	0.104	$O_{CH3O-}(4)$	0.055
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(1)$	0.035	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.036
J_3			
Ni(1)	1.742	Ni(4)	-0.012
$O_{CH3O-}(1)$	0.060	$O_{CH3O-}(2)$	0.037
$O_{CH3O-}(3)$	0.010	$O_{CH3O-}(4)$	0.063
$O_{CH3OH}(1)$	0.034	$O_{CH3OH}(4)$	-0.025
$O_{aldehyde}(1)$	0.276	$O_{phenoxy}(1)$	0.315
$O_{aldehyde}(4)$	-0.009	$O_{phenoxy}(4)$	0.043
J_4			
Ni(2)	1.723	Ni(3)	1.723
$O_{CH3O-}(1)$	0.104	$O_{CH3O-}(2)$	0.055
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(2)$	0.035	$O_{phenoxy}(2)$	0.036
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.036
J_5			
Ni(2)	1.723	Ni(4)	1.723
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.055	$O_{CH3O-}(4)$	0.104

$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(2)$	0.035	$O_{phenoxy}(2)$	0.036
$O_{aldehyde}(4)$	0.035	$O_{phenoxy}(4)$	0.036
J_6			
Ni(3)	1.724	Ni(4)	1.724
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.106	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(3)$	0.031	$O_{CH3OH}(4)$	0.031
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.035
$O_{aldehyde}(4)$	0.035	$O_{phenoxy}(4)$	0.035

[a]O_{CH3O-}(X) methoxy(X), O_{CH3OH}(X) methanol bonded to Ni(X), $O_{aldehyde}$(X) aldehyde oxygen bonded to Ni(X), $O_{phenoxy}$(X) phenoxy oxygen bonded to Ni(X).

Table S10. Mulliken spin densities computed for the high spin configuration of the optimized structure of [Ni_2] dimer models of compound **4**. See Figure S1 for labeling of atoms.

Atom Label[a]	Spin Density	Atom Label[a]	Spin Density
J_1			
Ni(1)	1.724	Ni(2)	1.724
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.052
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(2)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.036
J_2			
Ni(1)	1.723	Ni(3)	1.723
$O_{CH3O-}(1)$	0.106	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.103	$O_{CH3O-}(4)$	0.055
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.036
J_3			
Ni(1)	1.723	Ni(4)	1.723
$O_{CH3O-}(1)$	0.055	$O_{CH3O-}(2)$	0.104
$O_{CH3O-}(3)$	0.106	$O_{CH3O-}(4)$	0.052
$O_{CH3OH}(1)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(1)$	0.034	$O_{phenoxy}(1)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.037
J_4			
Ni(2)	1.724	Ni(3)	1.723
$O_{CH3O-}(1)$	0.103	$O_{CH3O-}(2)$	0.055
$O_{CH3O-}(3)$	0.052	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(3)$	0.032
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.034
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.036
J_5			
Ni(2)	1.723	Ni(4)	1.724
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.106
$O_{CH3O-}(3)$	0.054	$O_{CH3O-}(4)$	0.103

$O_{CH3OH}(2)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(2)$	0.034	$O_{phenoxy}(2)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.037
J_6			
Ni(3)	1.723	Ni(4)	1.724
$O_{CH3O-}(1)$	0.052	$O_{CH3O-}(2)$	0.052
$O_{CH3O-}(3)$	0.106	$O_{CH3O-}(4)$	0.106
$O_{CH3OH}(3)$	0.032	$O_{CH3OH}(4)$	0.032
$O_{aldehyde}(3)$	0.035	$O_{phenoxy}(3)$	0.036
$O_{aldehyde}(4)$	0.034	$O_{phenoxy}(4)$	0.036

[a]O_{CH3O-}(X) methoxy(X), O_{CH3OH}(X) methanol bonded to Ni(X), $O_{aldehyde}$(X) aldehyde oxygen bonded to Ni(X), $O_{phenoxy}$(X) phenoxy oxygen bonded to Ni(X).

Table S11. Mulliken spin densities computed for the high spin configuration of the experimental structure of [Ni_2] dimer models of compound **4**. See Figure S1 for labeling of atoms.

Atom Label[a]	Spin Density	Atom Label[a]	Spin Density
J_1			
Ni(1)	1.722	Ni(2)	1.720
$O_{CH3O-}(1)$	0.114	$O_{CH3O-}(2)$	0.113
$O_{CH3O-}(3)$	0.055	$O_{CH3O-}(4)$	0.056
$O_{CH3OH}(1)$	0.021	$O_{CH3OH}(2)$	0.019
$O_{aldehyde}(1)$	0.038	$O_{phenoxy}(1)$	0.039
$O_{aldehyde}(2)$	0.038	$O_{phenoxy}(2)$	0.037
J_2			
Ni(1)	1.723	Ni(3)	1.726
$O_{CH3O-}(1)$	0.110	$O_{CH3O-}(2)$	0.054
$O_{CH3O-}(3)$	0.110	$O_{CH3O-}(4)$	0.056
$O_{CH3OH}(1)$	0.021	$O_{CH3OH}(3)$	0.022
$O_{aldehyde}(1)$	0.037	$O_{phenoxy}(1)$	0.039
$O_{aldehyde}(3)$	0.036	$O_{phenoxy}(3)$	0.040
J_3			
Ni(1)	1.722	Ni(4)	1.722
$O_{CH3O-}(1)$	0.059	$O_{CH3O-}(2)$	0.109
$O_{CH3O-}(3)$	0.113	$O_{CH3O-}(4)$	0.054
$O_{CH3OH}(1)$	0.021	$O_{CH3OH}(4)$	0.023
$O_{aldehyde}(1)$	0.038	$O_{phenoxy}(1)$	0.039
$O_{aldehyde}(4)$	0.036	$O_{phenoxy}(4)$	0.040
J_4			
Ni(2)	1.721	Ni(3)	1.725
$O_{CH3O-}(1)$	0.108	$O_{CH3O-}(2)$	0.060
$O_{CH3O-}(3)$	0.056	$O_{CH3O-}(4)$	0.111
$O_{CH3OH}(2)$	0.019	$O_{CH3OH}(3)$	0.022
$O_{aldehyde}(2)$	0.038	$O_{phenoxy}(2)$	0.037
$O_{aldehyde}(3)$	0.036	$O_{phenoxy}(3)$	0.040
J_5			
Ni(2)	1.720	Ni(4)	1.722
$O_{CH3O-}(1)$	0.056	$O_{CH3O-}(2)$	0.114
$O_{CH3O-}(3)$	0.060	$O_{CH3O-}(4)$	0.109

O_{CH3OH}(2)	0.019	O_{CH3OH}(4)	0.023
$O_{aldehyde}$(2)	0.037	$O_{phenoxy}$(2)	0.037
$O_{aldehyde}$(4)	0.037	$O_{phenoxy}$(4)	0.040
J_6			
Ni(3)	1.726	Ni(4)	1.723
O_{CH3O-}(1)	0.053	O_{CH3O-}(2)	0.055
O_{CH3O-}(3)	0.115	O_{CH3O-}(4)	0.109
O_{CH3OH}(3)	0.022	O_{CH3OH}(4)	0.023
$O_{aldehyde}$(3)	0.037	$O_{phenoxy}$(3)	0.040
$O_{aldehyde}$(4)	0.037	$O_{phenoxy}$(4)	0.040

[a]O_{CH3O-}(X) methoxy(X), O_{CH3OH}(X) methanol bonded to Ni(X), $O_{aldehyde}$(X) aldehyde oxygen bonded to Ni(X), $O_{phenoxy}$(X) phenoxy oxygen bonded to Ni(X).

Table S12. Orbital contributions (%) to the spin densities

Orbital contributions to the spin densities, J_1					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(1)dz2	21.28	21.31	21.31	12.97	14.48
Ni(1)dx2-y2	3.42	3.73	4.07	18.25	19.01
Ni(1)dxy	18.10	17.80	17.46	0.27	0.22
Ni(2)dz2	21.28	21.31	21.31	14.98	14.29
Ni(2)dx2-y2	3.42	3.73	4.07	18.52	18.54
Ni(2)dxy	18.09	17.80	17.46	1.31	1.21
Orbital contributions to the spin densities, J_2					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(1)dz2	21.30	21.33	21.33	12.98	14.50
Ni(1)dx2-y2	3.42	3.72	4.06	18.27	19.04
Ni(1)dxy	18.07	17.78	17.44	0.27	0.22
Ni(3)dz2	21.30	21.33	21.33	15.30	15.77
Ni(3)dx2-y2	3.44	3.74	4.09	19.16	18.73
Ni(3)dxy	18.05	17.76	17.41	0.25	0.63
Orbital contributions to the spin densities, J_3					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(1)dz2	21.30	21.33	21.02	12.97	14.48
Ni(1)dx2-y2	3.44	3.74	4.90	18.24	19.00
Ni(1)dxy	18.05	17.76	17.32	0.27	0.22
Ni(4)dz2	21.30	21.33	-6.74	12.68	13.25
Ni(4)dx2-y2	3.42	3.72	1.25	17.35	18.09
Ni(4)dxy	18.07	17.78	5.36	1.24	0.44
Orbital contributions to the spin densities, J_4					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(2)dz2	21.30	21.33	21.33	14.95	14.25
Ni(2)dx2-y2	3.43	3.74	4.09	18.54	18.58
Ni(2)dxy	18.06	17.76	17.42	1.30	1.19

Ni(3)dz2	21.306	21.33	21.33	15.32	15.77
Ni(3)dx2-y2	3.41	3.72	4.07	19.15	18.72
Ni(3)dxy	18.08	17.78	17.43	0.25	0.64
Orbital contributions to the spin densities, J_5					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(2)dz2	21.30	21.33	21.33	14.93	15.82
Ni(2)dx2-y2	3.42	3.72	4.06	18.53	18.74
Ni(2)dxy	18.07	17.78	17.44	1.31	0.63
Ni(4)dz2	21.30	21.33	21.33	12.67	13.22
Ni(4)dx2-y2	3.44	3.74	4.09	17.37	18.10
Ni(4)dxy	18.05	17.75	17.41	1.26	0.46
Orbital contributions to the spin densities, J_6					
	1	**2**	**3**	**4opt.**	**4exp.**
Ni(3)dz2	21.28	21.31	21.31	15.34	15.82
Ni(3)dx2-y2	3.42	3.73	4.08	19.16	18.74
Ni(3)dxy	18.10	17.80	17.46	0.24	0.63
Ni(4)dz2	21.28	21.31	21.31	12.66	13.22
Ni(4)dx2-y2	3.42	3.73	4.07	17.35	18.10
Ni(4)dxy	18.10	17.80	17.46	1.26	0.46

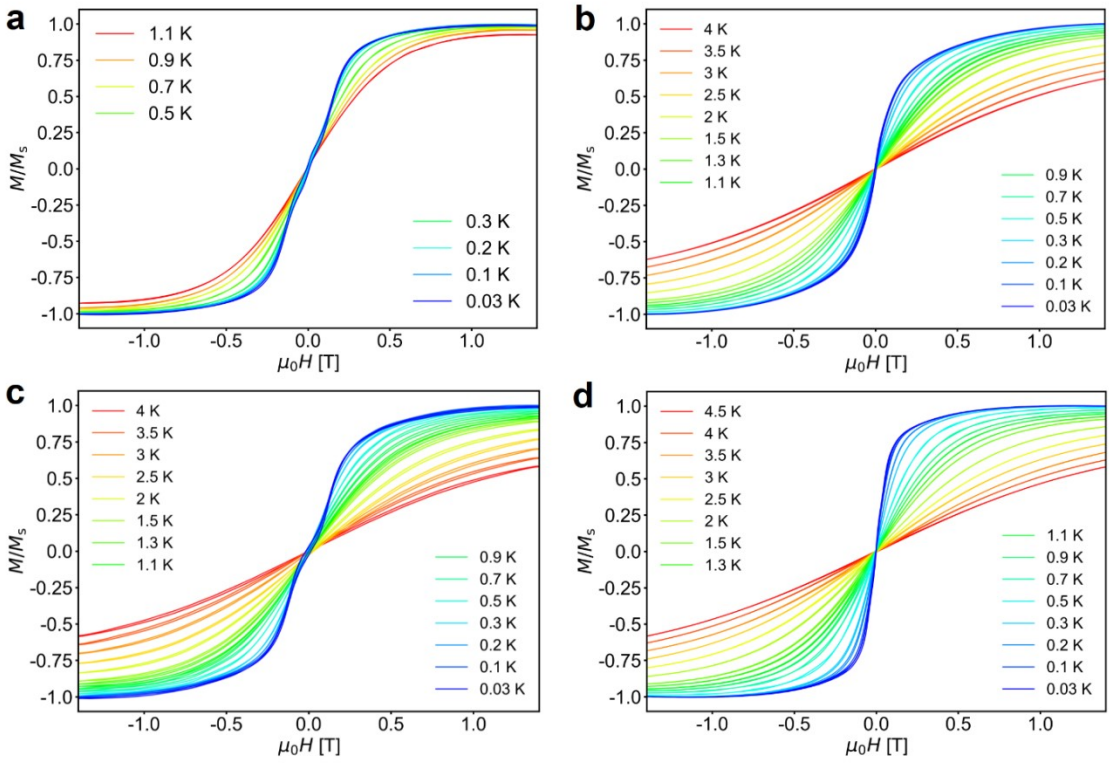

Figure S3. M(*H*) loops for a micron-sized single crystal of complexes (**a**) **1**; (**b**) **2**; (**c**) **3** and (**d**) **4**, measured by *μ*-SQUID at a field sweep rate = 8 mT/s and different bath temperatures.

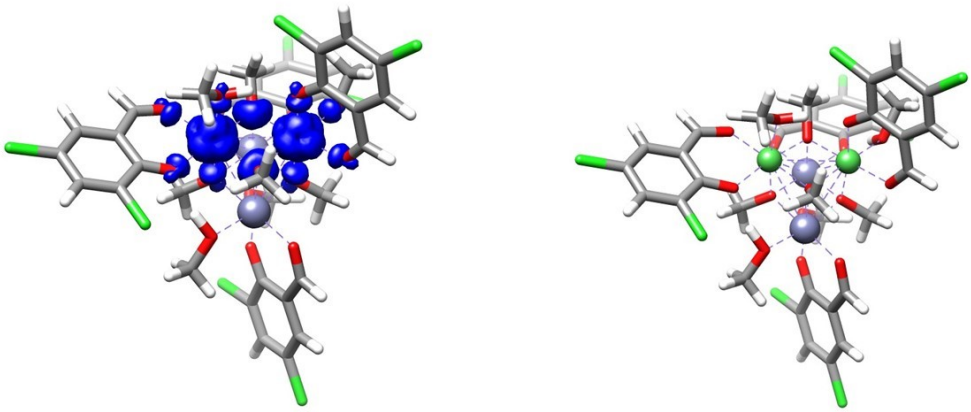

Figure S4. Graphical representation of the spin density (contour 0.004 e Å-3) at the ground-state (high-spin) configuration (left) and theoretical model used (right) of compound **1,** J_2.

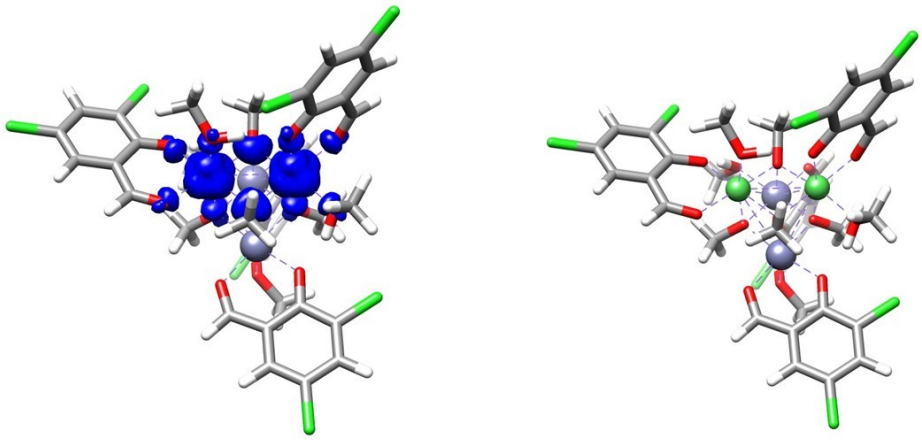

Figure S5. Graphical representation of the spin density (contour 0.004 e Å-3) at the ground-state (high-spin) configuration (left) and theoretical model used (right) of compound **1,** J_3.

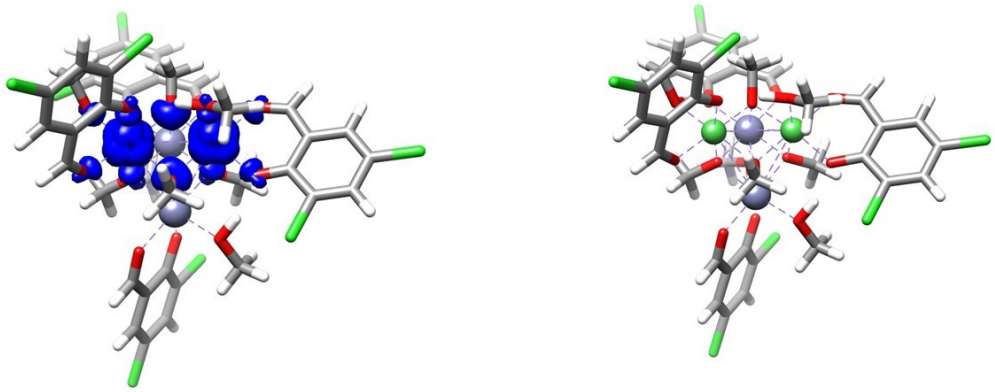

Figure S6. Graphical representation of the spin density (contour 0.004 e Å-3) at the ground-state (high-spin) configuration (left) and theoretical model used (right) of compound **1,** J_4.

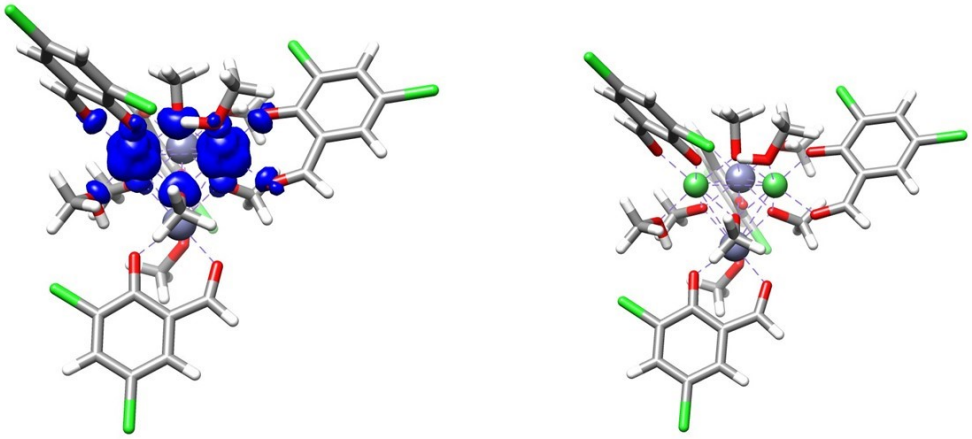

Figure S7. Graphical representation of the spin density (contour 0.004 e Å-3) at the ground-state (high-spin) configuration (left) and theoretical model used (right) of compound **1,** J_5.

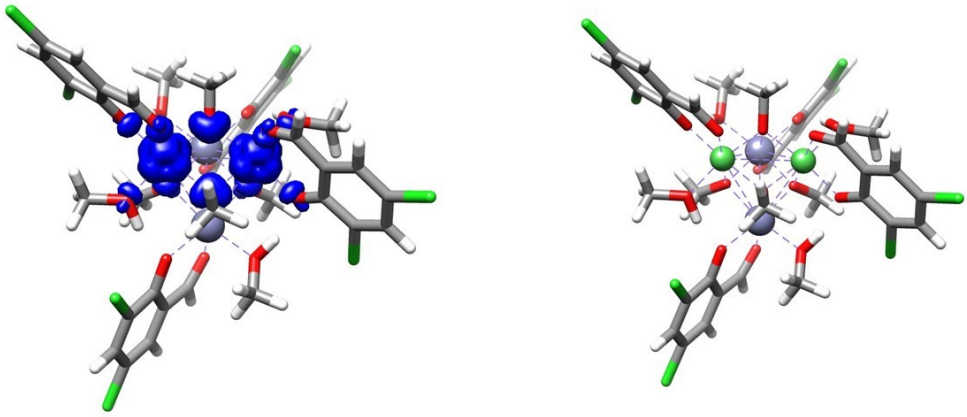

Figure S8. Graphical representation of the spin density (contour 0.004 e Å-3) at the ground-state (high-spin) configuration (left) and theoretical model used (right) of compound **1,** J_6.