Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The Structural Manipulation of a Series of Ni_4 Defective Dicubanes: Synthesis, X-ray Structures, Magnetic, and Computational Analyses.

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Content

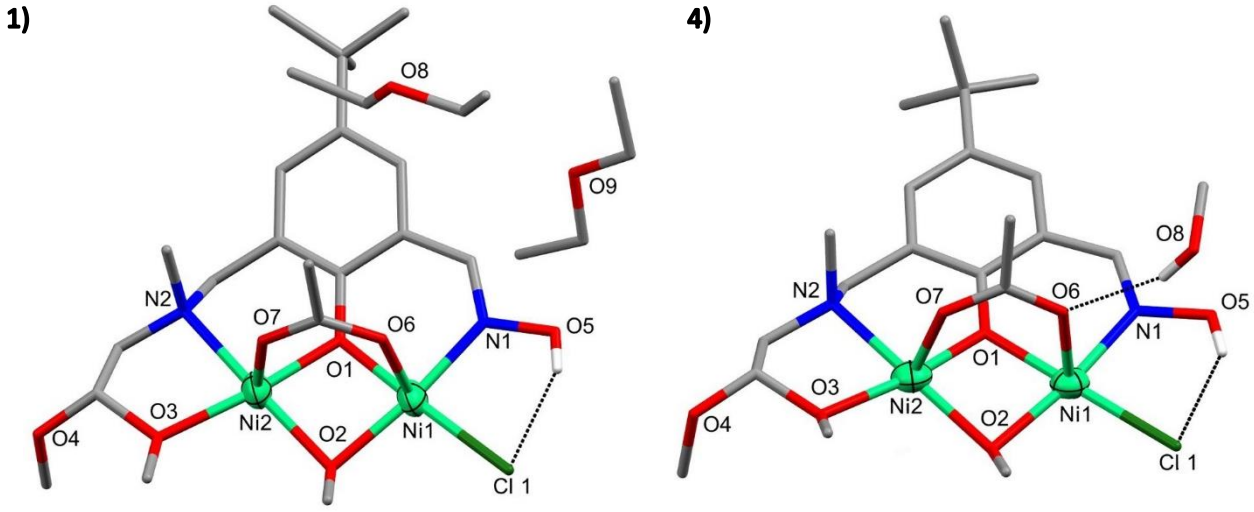

Figure S1: The asymmetric units of complexes **1** (left) and **4** (right) showing the free solvent molecules. No-interacting hydrogen atoms removed for clarity. Colour code: Ni = light green, N = blue, O = red, Cl = dark green, C = grey, and H = white. Hydrogen bonds represented as black dotted lines.

Table S1: Non-averaged bond lengths (Å) and bond angles (°) of **2** and **3**.

		2			
Ni1-Cl1	2.412(2)	Ni2-O2	2.080(5)	Ni3-O11	2.094(6)
Ni1-O2	2.091(5)	Ni2-O5	2.174(6)	Ni3-N3	2.046(7)
Ni1-O3	2.055(6)	Ni2-Cl3	2.377(3)	Ni4-Cl2	2.479(3)
Ni1-O4	2.015(5)	Ni2-N2	2.086(7)	Ni4-Cl4	2.371(3)
Ni1-O12	2.085(6)	Ni3-Cl2	2.401(2)	Ni4-O3	2.080(5)
Ni1-N1	2.054(7)	Ni3-O1	2.000(5)	Ni4-O4	2.037(6)
Ni2-Cl1	2.473(3)	Ni3-O2	2.073(6)	Ni4-O8	2.182(6)
Ni2-O1	2.020(6)	Ni3-O3	2.100(5)	Ni4-N4	2.104(7)
Ni1-O2-Ni3	95.51(7)	Ni1-O3-Ni3	95.77(7)	Ni1-Cl1-Ni2	86.68(8)
Ni3-Cl2-Ni4	86.91(8)	Ni2-O1-Ni3	100.75(6)	Ni1-O4-Ni4	99.96(6)
Ni1-O2-Ni2	106.95(5)	Ni3-O3-Ni4	106.84(5)	Ni2-O2-Ni3	96.38(7)
Ni1-O3-Ni4	97.25(7)				
		3			
Ni1-Cl1	2.283(6)	Ni2-O5	2.173(3)	Ni3-N3	2.014(4)
Ni1-F1	2.092(7)	Ni2-Cl3	2.369(2)	Ni4-Cl2	2.464(6)
Ni1-O2	2.058(3)	Ni2-F1	2.017(6)	Ni4-Cl4	2.351(2)
Ni1-O3	2.069(3)	Ni2-N2	2.089(3)	Ni4-F2	2.069(9)
Ni1-O4	2.005(3)	Ni3-Cl2	2.309(7)	Ni4-O3	2.092(3)
Ni1-O12	2.088(3)	Ni3-F2	2.122(10)	Ni4-O4	2.0214(3)
Ni1-N1	2.013(4)	Ni3-O1	2.019(3)	Ni4-O8	2.175(3)
Ni2-Cl1	2.506(5)	Ni3-O2	2.057(3)	Ni4-N4	2.090(4)
Ni2-O1	2.036(3)	Ni3-O3	2.051(3)	Ni1-O2-Ni3	95.02(11)
Ni2-O2	2.090(3)	Ni3-O11	2.117(3)	Ni1-O3-Ni3	94.90(11)
Ni1-Cl1-Ni2	84.29(12)	Ni3-Cl2-Ni4	85.35(16)	Ni1-F1-Ni2	103.06(5)
Ni3-F2-Ni4	101.13(5)	Ni2-O1-Ni3	99.99(13)	Ni1-O4-Ni4	99.29(12)
Ni1-O2-Ni2	101.73(10)	Ni3-O3-Ni4	102.78(11)	Ni2-O2-Ni3	96.34(11)
Ni1-O3-Ni4	95.73(12)				

Table S2: Crystal data and structural refinement details for **1-4**.

	1	**2**	**3**	**4**
Formula	$C_{52}H_{96}N_4O_{17}Cl_2Ni_4$	$C_{42}H_{78}N_4O_{13}Cl_4Ni_4$	$C_{42}H_{78}N_4O_{13}F_{1.2}Cl_{2.8}Ni_4$	$C_{42}H_{74}N_4O_{16}Cl_2Ni_4$
M_r (g mol^{-1})	1355.06	1223.72	1203.98	1196.74
***T* (K)**	120	123	183	123
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a* (Å)**	13.33(6)	10.16(11)	9.56(8)	10.94(8)
***b* (Å)**	13.86(7)	20.49(2)	21.05(14)	24.80(6)
***c* (Å)**	17.33(12)	25.79(3)	26.07(2)	10.14(3)
α (°)	90	90	90	90
β (°)	90.34	91.18(6)	90.15(6)	109.74(8)
γ (°)	90	90	90	90
***V* (Å^3)**	3205.7(3)	5371.6(11)	5253.1(7)	2593.7(2)
Z	2	1	1	2
ρcalc (g cm^{-3})	1.404	1.513	1.522	1.532
μ (mm^{-1})	2.628	3.907	3.471	3.154
***F* (000)**	1436.0	2568.0	2530.0	1256.0
2Θ Range for Data Collection/°	12.042 to 140.134	5.508 to 140.158	9.06 to 130.178	7.126 to 144.138
Index Ranges	-12≤h≤16, -15≤k≤16, -20≤l≤21	-11≤h≤12, -19≤k≤23, -31≤l≤30	-10≤h≤11, -23≤k≤24, -30≤l≤30	-13≤h≤13, -30≤k≤30, -10≤l≤12
Reflections Collected	45862	42778	37702	29026
Independent Reflections	5919 [R_{int} = 0.0852, R_{sigma} = 0.0431]	9809 [R_{int} = 0.2394, R_{sigma} = 0.4683]	8926 [R_{int} = 0.0727, R_{sigma} = 0.1558]	5013 [R_{int} = 0.1022, R_{sigma} = 0.0845]
Data/Restraints/Parameters	5919/51/386	9809/0/635	8926/3/646	5013/0/318
Goodness-of-Fit on F^2	1.044	0.863	1.151	1.125
Final R Indexes [$I > 2\sigma(I)$]	R_1 = 0.0580, wR_2 = 0.1593	R_1 = 0.0941, wR_2 = 0.1952	R_1 = 0.0581, wR_2 = 0.1645	R_1 = 0.0677, wR_2 = 0.1775
Final R Indexes [All Data]	R_1 = 0.0598, wR_2 = 0.1617	R_1 = 0.2708, wR_2 = 0.2526	R_1 = 0.1109, wR_2 = 0.1904	R_1 = 0.0853, wR_2 = 0.2100
Largest Diff. Peak/Hole /(e$^-$/Å^3)	0.88/-0.68	0.86/-0.96	1.02/-0.60	1.06/-1.09

Table S3: Ni-X-Ni angles (°) mediating the exchange interactions J_1, J_2, and J_3 in compounds **1-4**.

	Ni-μ$_3$O-Ni (Ni-μ$_2$O-Ni) / ° J_1	**Ni-μCl-Ni (Ni-μ$_3$O-Ni) / °** J_2	**Ni-μ$_3$O-Ni (Ni-μ$_3$O-Ni) / °** J_3
1	92.1 (95.4)	86.3 (111.3)	98.8 (98.8)
2	97.2 (99.9)	86.7 (107.0)	95.5 (95.8)
3	96.3 (99.3)	85.4* (101.8)	95.0 (94.9)
4	91.1 (94.8)	85.6 (107.8)	98.2 (98.2)

* Disordered Ni-F-Ni angle, 108.1°

Table S4. Spin configurations for complexes **1-4** used for estimating the magnetic exchange parameters.

Serial Number	***S***	**Spin configurations**			
		Ni1	**Ni2**	**Ni3**	**Ni4**
1	4	α	α	α	α
2	2	β	α	α	α
3	2	α	β	α	α
4	2	α	α	β	α
5	2	α	α	α	β
6	0	β	β	α	α
7	0	α	β	β	α
8	0	β	α	β	α

Table S5. Pertinent structural parameters for **1-4**.

Complex	**Exchange**	***avg* Ni-μ$_{2/3}$O/F/Cl-Ni angle (º)**	***avg* Ni-μ$_{2/3}$O/F/Cl distance (Å)**
1	J_1	93.7	2.019
	J_2	98.8	2.320
	J_3	98.8	2.077
2	J_1	98.6	2.043
	J_2	96.8	2.264
	J_3	95.7	2.080
3	J_1	97.8	2.051
	J_2	102.4	2.064
	J_3	95.0	2.059
4	J_1	93.0	2.037
	J_2	96.7	2.256
	J_3	98.2	2.065

Table S6. DFT computed overlap integrals for **1-4** on dimeric model complexes. The values highlighted in red suggest large magnetic orbital overlap and the values highlighted in yellow highlighted suggest moderate magnetic orbitals overlap. Both contribute to an antiferromagnetic interaction. The non-highlighted values represent orthogonal/weak magnetic orbital overlap which contribute to a ferromagnetic interaction.

Complex		***J*$_1$**			***J*$_2$**			***J*$_3$**	
	Ni(1)α/Ni(2)β	d_{z^2}	$d_{x^2-y^2}$	Ni(2)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$	Ni(1)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$
1	d_{z^2}	0.041	0.015	d_{z^2}	0.022	0.034	d_{z^2}	0.005	0.022
	$d_{x^2-y^2}$	0.005	0.006	$d_{x^2-y^2}$	0.028	0.036	$d_{x^2-y^2}$	0.022	0.043
	Ni(1)α/Ni(2)β	d_{z^2}	$d_{x^2-y^2}$	Ni(2)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$	Ni(1)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$
2	d_{z^2}	0.011	0.028	d_{z^2}	0.001	0.022	d_{z^2}	0.007	0.009
	$d_{x^2-y^2}$	0.061	0.011	$d_{x^2-y^2}$	0.024	0.035	$d_{x^2-y^2}$	0.013	0.019
	Ni(1)α/Ni(2)β	d_{z^2}	$d_{x^2-y^2}$	Ni(2)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$	Ni(1)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$
3	d_{z^2}	0.024	0.016	d_{z^2}	0.036	0.061	d_{z^2}	0.001	0.016
	$d_{x^2-y^2}$	0.012	0.050	$d_{x^2-y^2}$	0.006	0.006	$d_{x^2-y^2}$	0.012	0.018
	Ni(1)α/Ni(2)β	d_{z^2}	$d_{x^2-y^2}$	Ni(2)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$	Ni(1)α/Ni(3)β	d_{z^2}	$d_{x^2-y^2}$
4	d_{z^2}	0.041	0.027	d_{z^2}	0.004	0.023	d_{z^2}	0.011	0.009
	$d_{x^2-y^2}$	0.004	0.004	$d_{x^2-y^2}$	0.019	0.055	$d_{x^2-y^2}$	0.009	0.044

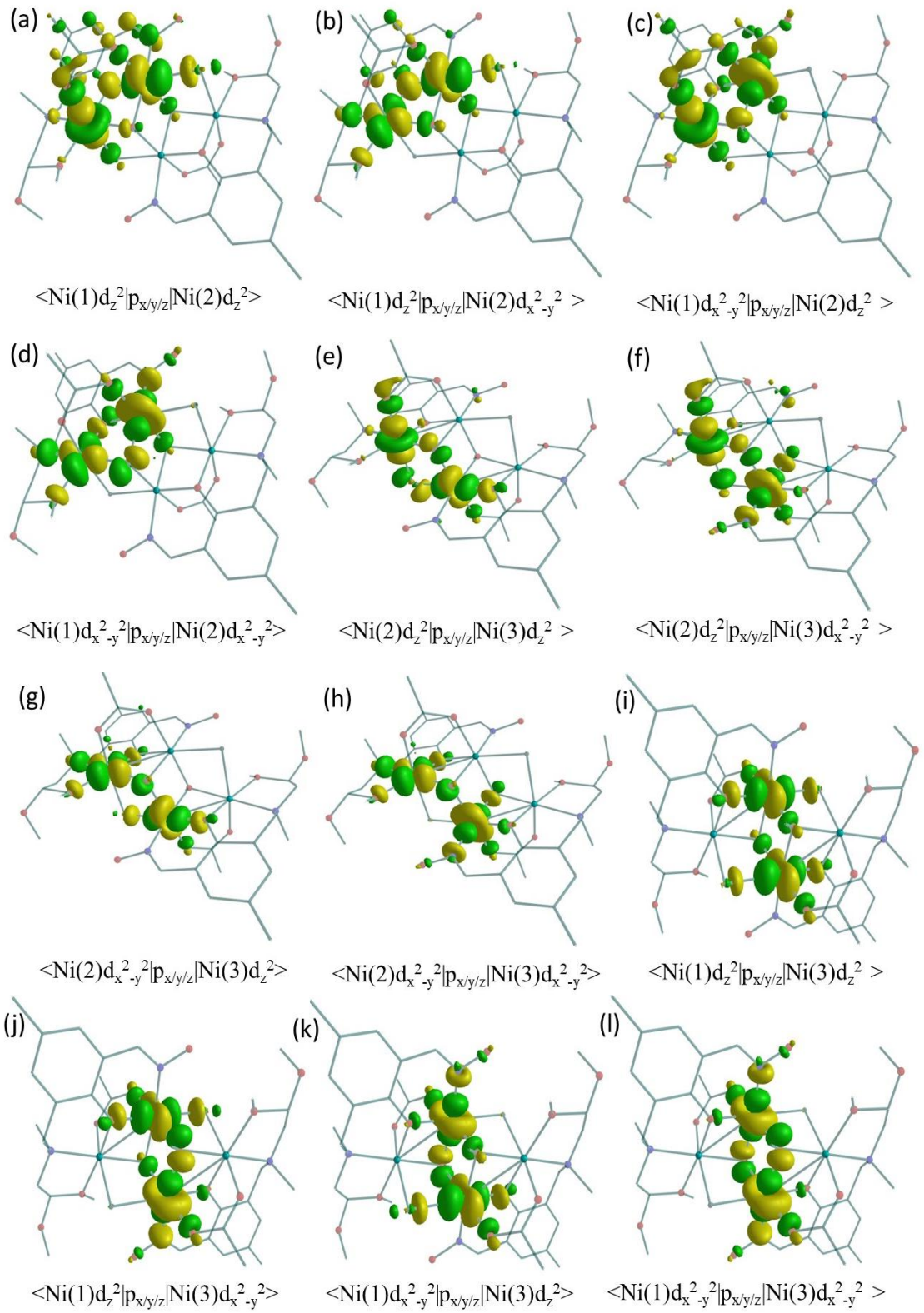

Figure S2. Representative figures showing SOMO(s)-SOMO(s) interactions.

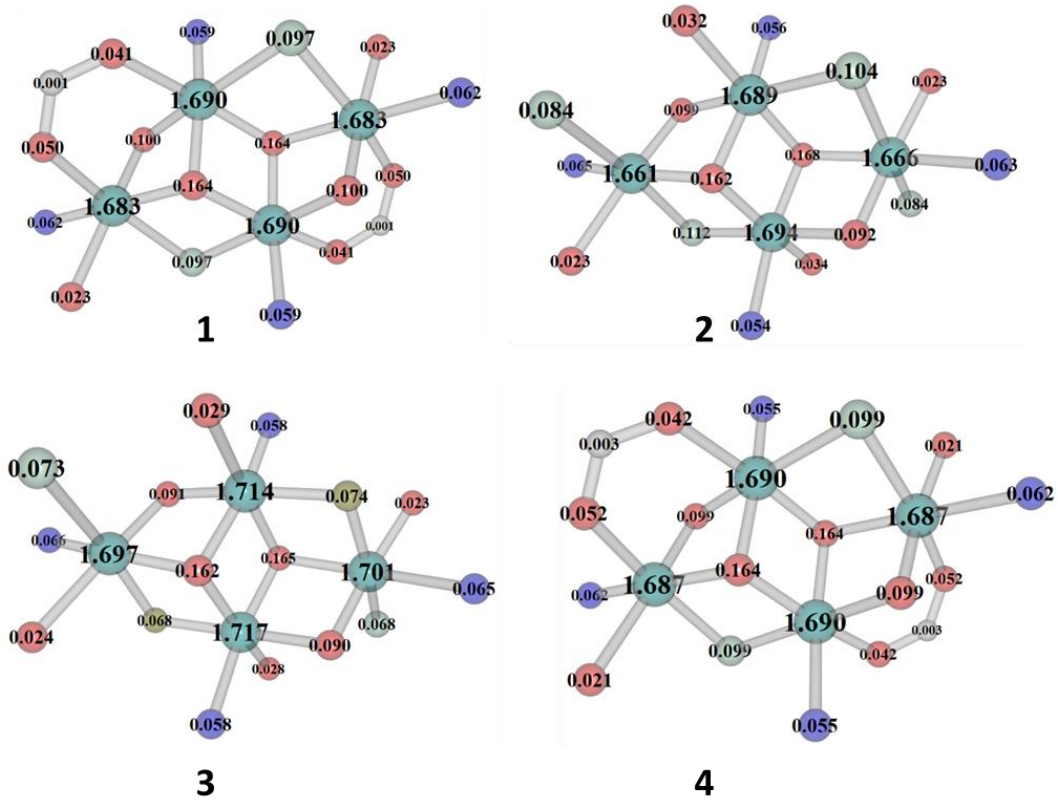

Figure S3. DFT computed spin density values on selected atoms for **1**-**4**.