Electronic Supplementary Information

High Nuclearity Ni(II) Cages from Hydroxamate ligands

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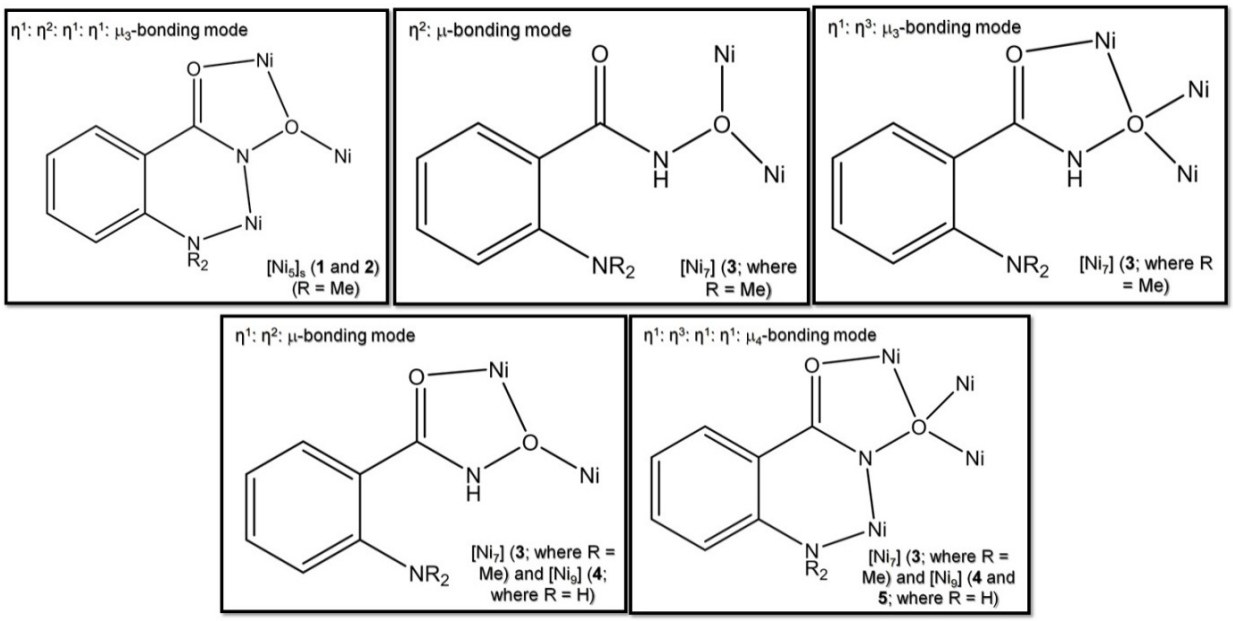


Figure S1 Schematic representing the various bonding modes exhibited by the hydroxamate ligands utilised in this work.

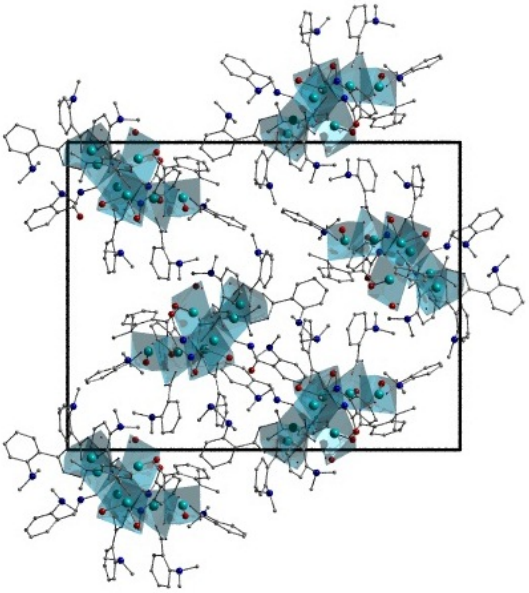


Figure S2 Crystal packing observed along the *a* direction of the unit cell axis in **3**. All hydrogen atoms, waters of crystallisation and SO_4^{2-} counter anions have been omitted for clarity.

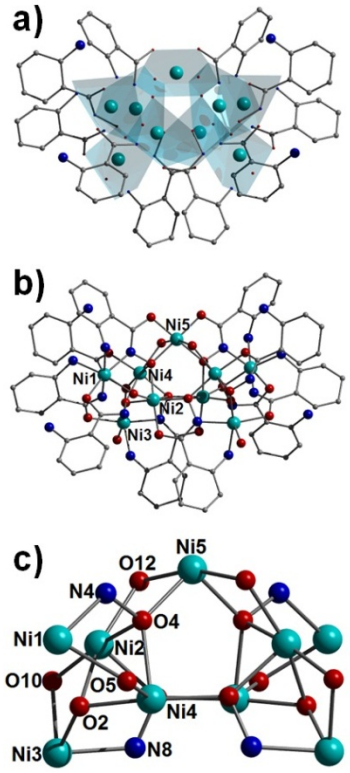


Figure S3 Polyhedral (a) and regular (b) representation of the crystal structure in **4**. (c) Metallic core in **4**. Colour code as in Figure 1. Hydrogen atoms have been omitted for clarity.

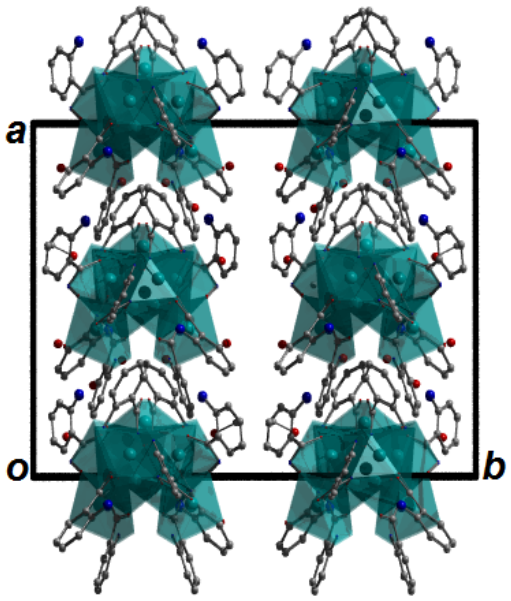
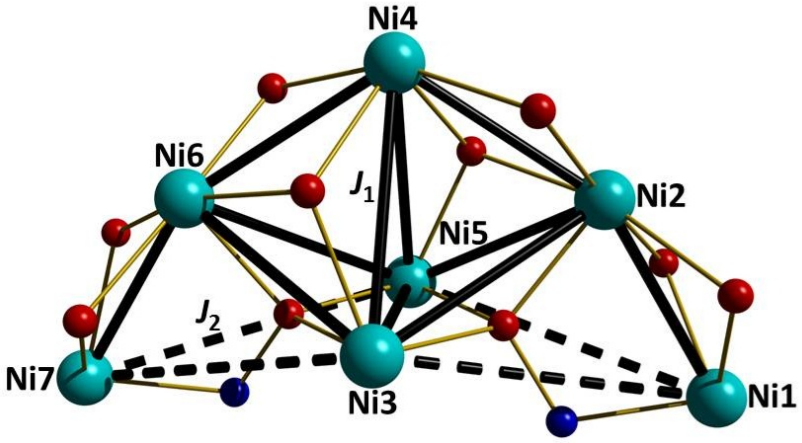


Figure S4 Packing motif in the unit cell of **5** as viewed down the *c* unit cell direction. All hydrogen atoms, perchlorate counter anions and waters of crystallisation have been omitted for clarity.



$$\hat{H}_{ex} = -2J_1 (\hat{S}_{Ni1}\cdot\hat{S}_{Ni2} + \hat{S}_{Ni2}\cdot\hat{S}_{Ni3} + \hat{S}_{Ni2}\cdot\hat{S}_{Ni4} + \hat{S}_{Ni2}\cdot\hat{S}_{Ni5} + \hat{S}_{Ni3}\cdot\hat{S}_{Ni4} + \hat{S}_{Ni3}\cdot\hat{S}_{Ni5} + \hat{S}_{Ni3}\cdot\hat{S}_{Ni6} + \hat{S}_{Ni4}\cdot\hat{S}_{Ni5} + \hat{S}_{Ni4}\cdot\hat{S}_{Ni6} + \hat{S}_{Ni5}\cdot\hat{S}_{Ni6} + \hat{S}_{Ni6}\cdot\hat{S}_{Ni7}) - 2J_2(\hat{S}_{Ni1}\cdot\hat{S}_{Ni3} + \hat{S}_{Ni1}\cdot\hat{S}_{Ni5} + \hat{S}_{Ni3}\cdot\hat{S}_{Ni7} + \hat{S}_{Ni5}\cdot\hat{S}_{Ni7})$$

Figure S5 Schematic illustrating the model used to fit the experimental data for complex **3**. See main text for fitting parameters.

Table S1 Various accessible spin projections for complex **1**. Key: Orange sphere (S = 0), red arrow (S = -1) and black arrow (S =1).

	Ni1(Oct.)	Ni2(Sq. Plnr)	Ni3(Sq. Pyr)	Ni4(Sq. Plnr)	Ni5(Sqr Pyr)	TOTAL **S**	ENERGY(KJ/mol)
Ni5-MEOH-3S						3	0.966972
BS-3S-1						1	0.916037
BS-3S-2						1	0.954894
BS-3S-3						1	0

Table S2 Various accessible spin projections for complex **2**. Key: Orange sphere (S = 0), red arrow (S = -1) and black arrow (S =1).

	Ni1(Sqr pyr)	Ni2(Sq. Pyr)	Ni3(Sq. Pyr)	Ni4(Sq. Plnr)	Ni5(Oct.)	TOTAL **S**	ENERGY (KJ/mol)
Ni5-Py-4S-1						4	2.82477545
BS-4S-1						2	1.07094145
BS-4S-2						2	0
BS-4S-3						2	2.25661725
BS-4S-4						2	2.25661725
BS-4S-5						0	0.82046875
BS-4S-6						0	0.16881965

Table S3 Calculated overlap integrals for complex **1**.

Alpha/Beta	**Ni3-$d_{x^2-y^2}$**	**Ni3-d_{z^2}**	**Ni5-$d_{x^2-y^2}$**	**Ni5-d_{z^2}**
Ni1-$d_{x^2-y^2}$	0.11	0.10	0.11	0.10
Ni1-d_{z^2}	0.04	0.06	0.04	0.06

Table S4 Calculated overlap integrals for complex **2**.

Alpha/Beta	**Ni3-d_{z^2}**	**Ni3-$d_{x^2-y^2}$**	**Ni2-d_{z^2}**	**Ni2-$d_{x^2-y^2}$**	**Ni5-d_{z^2}**	**Ni5-$d_{x^2-y^2}$**
Ni1-d_{z^2}	0.04	0.02	0.07	0.17	0.02	0.02
Ni1-$d_{x^2-y^2}$	0.06	0.22	0.06	0.24	0.10	0.01
Ni3-d_{z^2}			0.09	0.06		
Ni3-$d_{x^2-y^2}$			0.03	0.22		
Ni5-d_{z^2}			0.05	0.23		
Ni5-$d_{x^2-y^2}$			0.04	0.10		

Table S5 Selected structural parameter corresponding to the computed *J* values for **2**.

Calculated *J* constants	**Ni-O-Ni Angle (˚)**	**Ni-N-O-Ni Dihedral**	**Ni-Ni Distance (Å)**
J_{1A}	114	14	3.3
J_{1B}	121	16	3.4
J_{1C}	115	32	3.3
J_{2A}	-----	176	4.7
J_{2B}	-----	165	4.8