

## Supplementary Material

# Exploring the Potential of Oxalyldihydrazide-Derived Schiff Bases as Versatile Ligands: Synthesis, Structural Characterization and Magnetic Properties

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Table S1. Crystallographic data for compounds 1–5.

Compound	1	2	3	4	5
Formula	C <sub>30</sub> H <sub>44</sub> Cu <sub>5</sub> N <sub>18</sub> O <sub>32</sub>	C <sub>70</sub> H <sub>64</sub> Mn <sub>2</sub> N <sub>12</sub> O <sub>12</sub>	C <sub>54</sub> H <sub>45</sub> N <sub>12</sub> NiO <sub>32</sub>	C <sub>108</sub> H <sub>90</sub> N <sub>24</sub> Ni <sub>4</sub> O <sub>11</sub>	C <sub>80</sub> H <sub>104</sub> N <sub>24</sub> Ni <sub>8</sub> O <sub>36</sub>
M.W. [g·mol <sup>-1</sup> ]	1485.98	1375.21	1016.73	2135.88	2447.55
System	Triclinic	Triclinic	Triclinic	Monoclinic	Tetragonal
Space group	P-1	P-1	P-1	C2/c	I41/a
<i>a</i> [Å]	10.1076(9)	11.3329(6)	10.5553(5)	26.793(3)	29.072(2)
<i>b</i> [Å]	11.2497(10)	11.5931(5)	13.3523(7)	29.651(3)	29.072(2)
<i>c</i> [Å]	13.1681(12)	12.6704(6)	19.1747(9)	17.2671(17)	15.737(2)
$\alpha$ [°]	79.238(3)	100.398(2)	89.912(2)	90	90
$\beta$ [°]	70.788(3)	90.317(2)	75.860(2)	118.777(3)	90
$\gamma$ [°]	63.365(3)	94.400(2)	68.974(2)	90	90
<i>V</i> [Å <sup>3</sup> ]	1262.5(2)	1632.20(14)	2435.0(2)	12024(2)	13301(3)
<i>Z</i>	4	1	2	4	4
<i>T</i> [K]	100(2)	100(2)	100(2)	100(2)	100(2)
$\lambda(\text{Mo-K}\alpha)$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho$ calcd. [Mg cm <sup>-3</sup> ]	1.954	1.399	1.387	1.180	1.222
$\mu$ [mm <sup>-1</sup> ]	2.191	0.460	0.464	0.679	1.178
<i>R</i> (reflections)	0.0485(3905)	0.0536(8650)	0.0649(12474)	0.1127(7105)	0.0798(4155)
<i>wR</i> <sup>2</sup> (reflections)	0.1178(5184)	0.1494(10043)	0.1629(14988)	0.3494(12388)	0.2489(6860)
CCDC numbers <sup>[a]</sup>	2390280	2390353	2390354	2390355	2390303

<sup>[a]</sup> CCDC numbers contain supplementary crystallographic data for 1–5. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>

**Table S2.** Selected bond lengths (Å) and angles (°) for compound 1.

Atom	Distance [Å]	Atom	Angle (°)
Cu(1)–N(3)	1.943(3)	N(3)–Cu(1)–N(4)	79.89(14)
Cu(1)–N(4)	1.991(3)	N(3)–Cu(1)–N(1)	91.66(15)
Cu(1)–N(1)	2.001(4)	N(3)–Cu(1)–O(3w)	147.88(16)
Cu(1)–O(3w)	2.014(3)	N(3)–Cu(1)–O(3)	124.41(14)
Cu(1)–O(3)	2.217(3)	N(5)–Cu(2)–N(6)	80.42(15)
Cu(2)–O(4w)	1.922(3)	N(5)–Cu(2)–O(2)	79.07(13)
Cu(2)–N(5)	1.934(4)	N(2)–Cu(3)–O(1)	82.07(13)
Cu(2)–N(6)	2.029(4)	N(2)–Cu(3)–O(1S)	90.42(16)
Cu(2)–O(2)	2.064(3)	O(1)–Cu(3)–O(1S)	94.68(14)
Cu(2)–O(1w)	2.422(5)	N(3)–Cu(1)–N(4)	79.89(14)
Cu(3)–N(2)	1.964(3)	N(3)–Cu(1)–N(1)	91.66(15)
Cu(3)–O(1)	2.003(3)	N(3)–Cu(1)–O(3w)	147.88(16)
Cu(3)–O(1S)	2.310(4)	N(3)–Cu(1)–O(3)	124.41(14)
		N(5)–Cu(2)–N(6)	80.42(15)

**Table S3.** Selected bond lengths (Å) and angles (°) for compound 2.

Atom	Distance [Å]	Atom	Angle (°)
Mn(1)–N(1)	2.281(15)	N(1)–Mn(1)–N(2)	69.61(5)
Mn(1)–N(2)	2.3201(15)	N(2)–Mn(1)–O(1)	67.00(5)
Mn(1)–O(1)	2.169(14)	O(1)–Mn(1)–O(1)′	68.47(6)
Mn(1)–O(1)′	2.216(14)	O(1)–Mn(1)–O(2)	67.02(5)
Mn(1)–O(2)	2.572(2)	O(2)–Mn(1)–N(1)	88.38(5)
Mn(1)–O(3)	2.188(16)	Mn(1)–O(1)–Mn(1)′	111.53(7)
Mn(1)–O(4)	2.096(15)		
Mn(1)⋯Mn(1)′	3.6255(4)		

(′): 1 – x, 1 – y, 2 – z

**Table S4.** Selected bond lengths (Å) and angles (°) for compound 3.

Atom	Distance [Å]	Atom	Angle (°)
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Ni(1)–N(1)	2.091(2)	N(1)–Ni(1)–N(2)	78.38(7)
Ni(1)–N(2)	1.9868(18)	N(7)–Ni(1)–N(8)	78.73(8)
Ni(1)–N(7)	2.104(2)		
Ni(1)–N(8)	1.9909(18)		
Ni(1)–O(1)	2.1009		
Ni(1)–O(3)	2.0768(16)		

**Table S5.** Selected bond lengths (Å) and angles (°) for compound **4**.

Atom	Distance [Å]	Atom	Angle (°)
Ni(1)–N(1)	2.083(6)	N(1)–Ni(1)–N(2)	77.67(7)
Ni(1)–N(2)	1.988(6)	N(11)–Ni(1)–N(12)	78.07(3)
Ni(1)–N(11)	1.997(6)	N(5)–Ni(2)–N(6)	77.41(3)
Ni(1)–N(12)	2.083(7)	N(7)–Ni(2)–N(8)	77.94(3)
Ni(1)–O(2)	2.103(5)		
Ni(1)–O(4)	2.141(5)		
Ni(2)–N(5)	1.995(8)		
Ni(2)–N(6)	2.051(8)		
Ni(2)–N(7)	2.059(7)		
Ni(2)–N(8)	1.984(7)		
Ni(2)–O(1)	2.104(5)		
Ni(2)–O(3)	2.099(5)		
Ni(1)···Ni(2)	6.861(2)		
Ni(1)···Ni(2)'	6.913(2)		

('): 1 – x, y, 1/2 – z

**Table S6.** Selected bond lengths (Å) and angles (°) for compound **5**.

Atom	Distance [Å]	Atom	Angle (°)
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Ni(1)–N(3)	2.075(6)	N1–Ni1–N2	78.07(2)
Ni(1)–N(4)	2.101(5)	N5–Ni1–N6	78.26(2)
Ni(1)–O(3)	2.091(6)	Ni(1)–N(4)–N(5)–Ni(2)	166.6(4)
Ni(1)–O(4)	2.053(6)	Ni(2)–N(2)–N(3)–Ni(2)	176.2(3)
Ni(1)–O(5)	2.098(7)		
Ni(1)–O(6)	2.032(5)		
Ni(2)–N(1)	2.134(5)		
Ni(2)–N(2)	1.993(6)		
Ni(2)–N(5)	1.981(6)		
Ni(2)–N(6)	2.130(6)		
Ni(2)–O(1)	2.093(4)		
Ni(2)–O(2)	2.087(4)		
Ni(1)···Ni(2)	4.981(2)		
Ni(2)···Ni(1)′	4.966(2)		
Ni(2)···Ni(2)′′	6.822(2)		

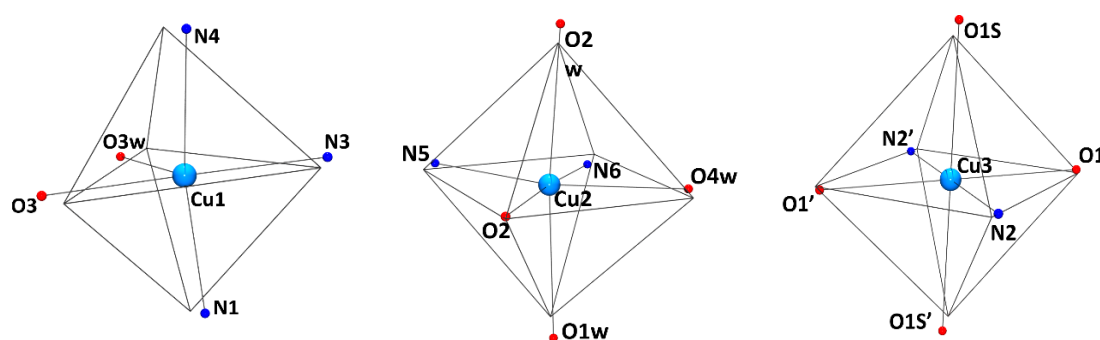
(′):  $1/4 + y, 3/4 - x, 3/4 - z$       (′′):  $3/4 - y, -1/4 + x, 3/4 - z$

# SHAPE:

- Shape measures calculation performed for different metal ions in **1–5** are reported in the following Tables S7-S11 where  $S(P) = 0$  corresponds to a structure fully coincident in shape with the reference polyhedron P, regardless of size and orientation.
- The ideal  $ML_5$ ,  $ML_6$  and  $ML_7$  polyhedra verified are:  
**For ideal  $ML_5$  polyhedra:** PP-5 (D5h) Pentagon; vOC-5 (C4v) Vacant octahedron; TBPY-5 (D3h) Trigonal bipyramid; SPY-5 (C4v) Spherical square pyramid; JTBPY-5 (D3h) Johnson trigonal bipyramid J12  
**For ideal  $ML_6$  polyhedra:** HP-6 (D6h) Hexagon; PPY-6 (C5v) Pentagonal pyramid; OC-6 (Oh) Octahedron; TPR-6 (D3h) Trigonal prism; JPPY-6 (C5v) Johnson pentagonal pyramid J2  
**For Ideal  $ML_7$  polyhedra:** HP-7 (D7h) Heptagon; HPY-7 (C6v) Hexagonal pyramid; PBPY-7 (D5h) Pentagonal bipyramid; COC-7 (C3v) Capped octahedron; CTPR-7 (C2v) Capped trigonal prism; JPBPY-7 (D5h) Johnson pentagonal bipyramid J13; JETPY-7 (C3v) Johnson elongated triangular pyramid J7
- The closest polyhedron is highlighted in bold and star symbol for each metal ion.

**Table S7.** Shape measures calculation for the Cu1, Cu2 and Cu3 cations with, penta- and hexacoordination environment of **1**.

Cu1 (CN = 5)		Cu2 (CN = 6)		Cu3 (CN = 6)	
S(PP-5)	25.84	S(HP-6)	33.03	S(HP-6)	28.96
S(vOC-5)	4.25	S(PPY-6)	24.36	S(PPY-6)	27.84
<b>S(TBPY-5)*</b>	<b>3.41</b>	<b>S(OC-6)*</b>	<b>2.06</b>	<b>S(OC-6)*</b>	<b>0.95*</b>
S(SPY-5)	3.54	S(TPR-6)	12.88	S(TPR-6)	16.05
S(JTBPY-5)	6.26	S(JPPY-6)	27.86	S(JPPY-6)	30.49



**Figure S1.** Coordination environments of cations Cu1, Cu2 and Cu3 in compound **1**

**Table S8.** Shape measures calculation for the Mn cation with both, hexa- and heptacoordination environment of **2**.

Mn1 (CN = 6)		Mn1 (CN = 7)	
S(HP-6)	29.46	S(HP-7)	31.44
S(PPY-6)	14.92	S(HPY-7)	20.92
S(OC-6)	9.20	<b>S(PBPY-7)*</b>	<b>1.50*</b>
<b>S(TPR-6)*</b>	<b>6.26*</b>	S(COC-7)	6.13
S(JPPY-6)	18.67	S(CTPR-7)	5.01
		S(JPBPY-7)	3.90
		S(JETPY-7)	20.87

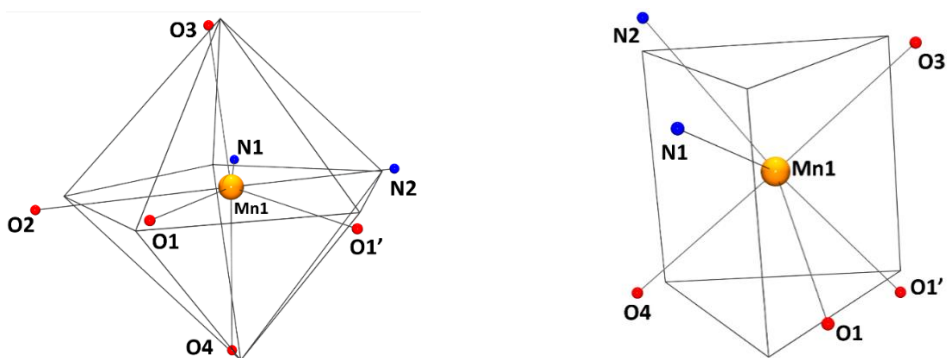


Figure S2. Coordination environments of cations Mn1 in compound 2

Table S9. Shape measures calculation for the Ni cation of complex 3.

Ni (CN = 6)	
S(HP-6)	34.33
S(PPY-6)	21.34
<b>S(OC-6)*</b>	<b>3.20*</b>
S(TPR-6)	10.38
S(JPPY-6)	25.37

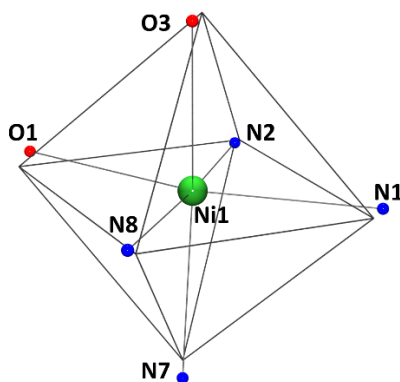


Figure S3. Coordination environments of cation Ni in compound 3

Table S10. SHAPE measurements for the Ni1 and Ni2 cations of complex 4.

Ni1 (CN = 6)		Ni2 (CN = 6)	
S(HP-6)	32.23	S(HP-6)	33.92
S(PPY-6)	20.86	S(PPY-6)	21.55
<b>S(OC-6)*</b>	<b>3.48*</b>	<b>S(OC-6)*</b>	<b>3.11*</b>
S(TPR-6)	10.76	S(TPR-6)	11.01
S(JPPY-6)	20.64	S(JPPY-6)	25.37

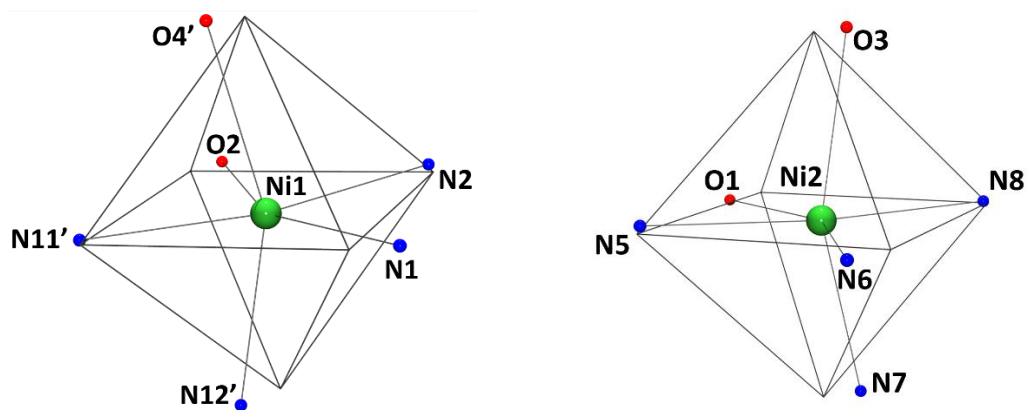


Figure S4. Coordination environments of Ni1 and Ni2 cations in compound 4

Table S11. Shape measures calculation for the Ni1 and Ni2 cations of complex 5.

Ni1 (CN = 6)		Ni2 (CN = 6)	
S(HP-6)	30.21	S(HP-6)	33.19
S(PPY-6)	27.00	S(PPY-6)	21.65
<b>S(OC-6)*</b>	<b>0.48*</b>	<b>S(OC-6)*</b>	<b>3.72*</b>
S(TPR-6)	15.32	S(TPR-6)	9.11
S(JPPY-6)	30.27	S(JPPY-6)	25.11

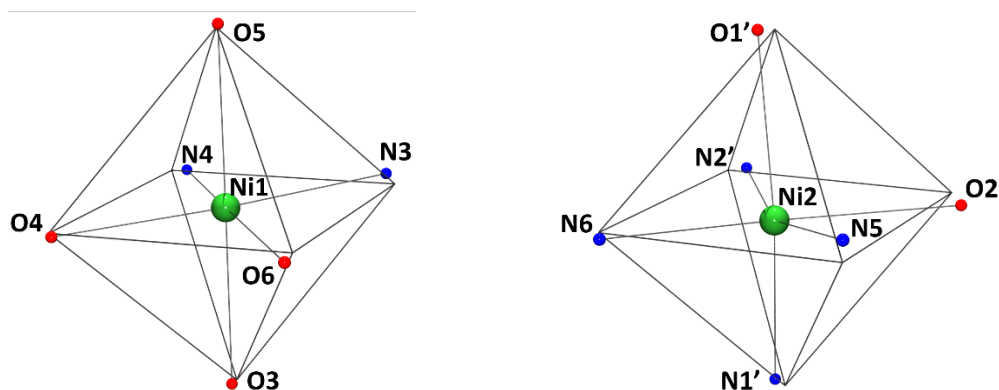
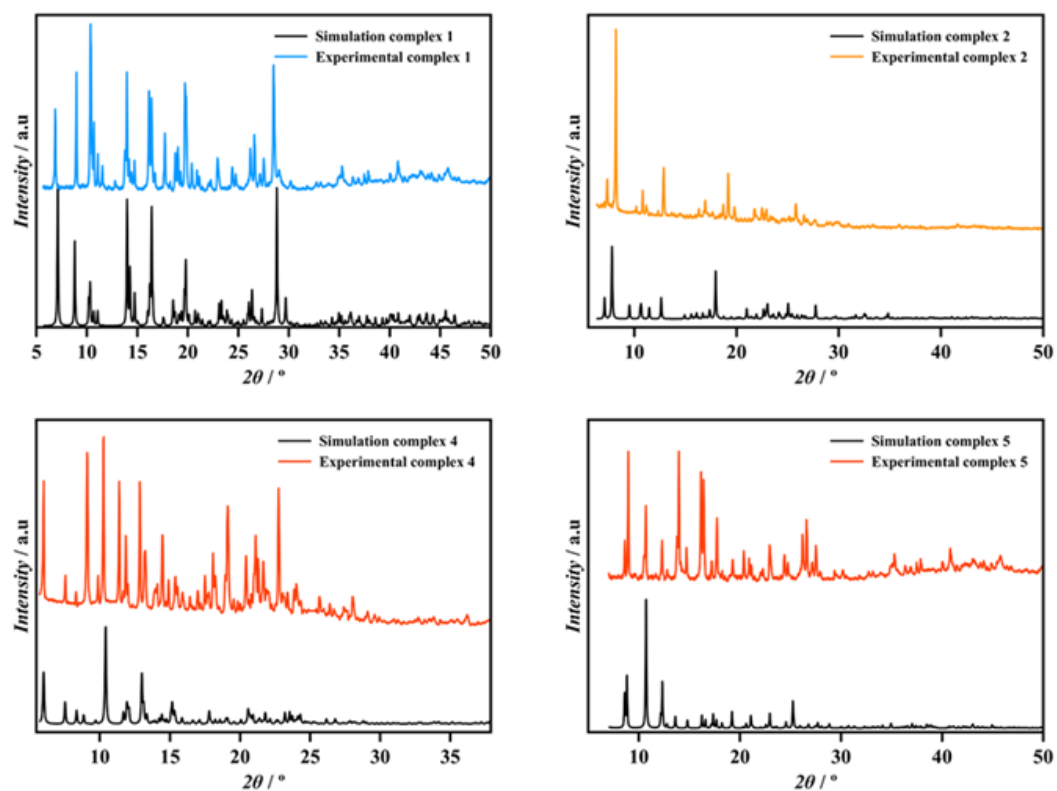


Figure S5. Coordination environments of Ni1 and Ni2 cations in compound 5



**Figure S6.** Experimental and simulation Powder X-ray Diffraction (PXRD) patterns for compounds 1, 2, 4 and 5.