High-spin Ni(II) clusters: triangles and planar tetranuclear complexes

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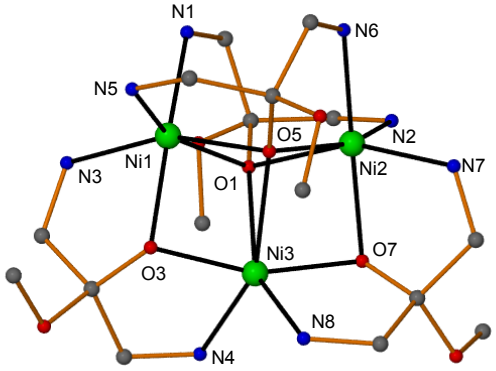

Fig. S1 The molecular structure of complex **4**. Most carbon and all hydrogen atoms have been omitted for clarity.

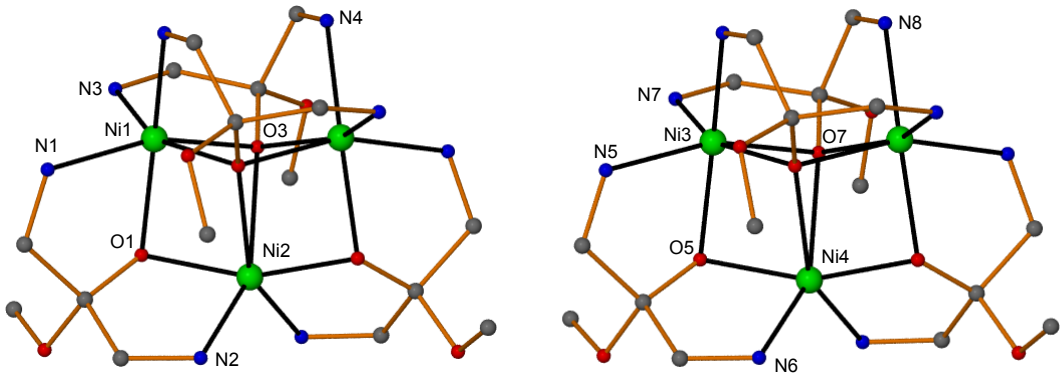

Fig. S2 The structures of the two [Ni_3] triangles found in the crystal structure of complex **5**. Most carbon and all hydrogen atoms have been omitted for clarity.

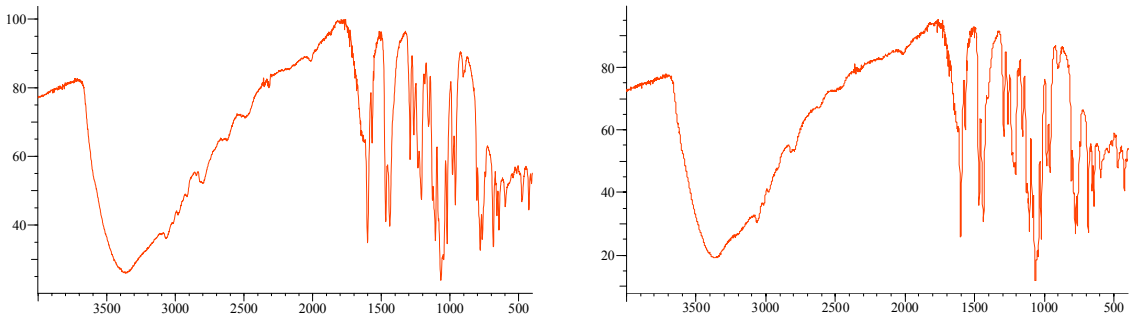

Fig. S3 The IR spectra (KBr disks) of complex **1** (left) and **2** (right) in the 4000 – 400 cm^{-1} region.

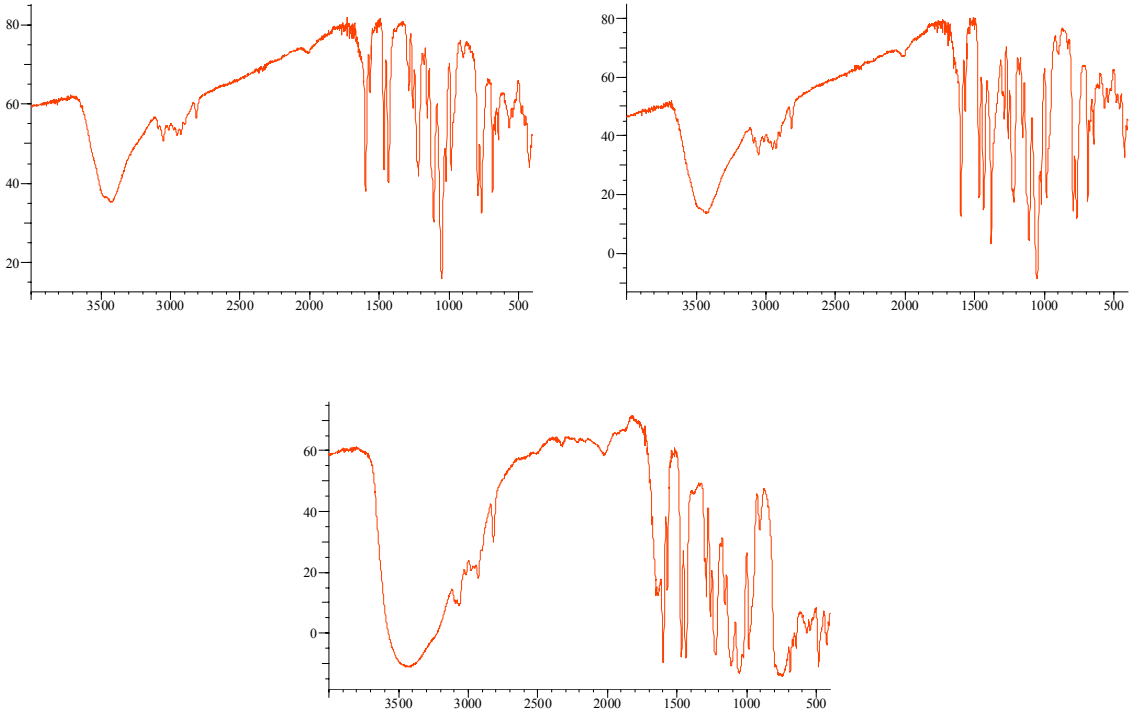

Fig. S4 The IR spectra (KBr disks) of complex **3** (top left), **4** (top right) and **5** (bottom) in the 4000 – 400 cm^{-1} region.

Table S1 Selected interatomic distances (Å) and angles (°) for complex **1**.[a]

Ni1···Ni2	3.374	Ni1···Ni2#1	3.101
Ni1···Ni1#1	5.663	Ni2···Ni2#1	3.151
Ni1–O3	2.019 (2)	Ni2–O1#1	2.028 (2)
Ni1–N2	2.070 (3)	Ni2–N4#1	2.042 (3)
Ni1–N3	2.089 (3)	Ni2–N1#1	2.092 (3)
Ni1–O5	2.134 (3)	Ni2–O1	2.106 (2)
Ni1–O1	2.165 (2)	Ni2–O3#1	2.126 (2)
Ni1–Cl1	2.4051 (11)	Ni2–Cl1	2.4275 (10)
O3–Ni1–N2	156.68 (11)	O1#1–Ni2–N4#1	158.76 (11)
O3–Ni1–N3	78.77 (11)	O1#1–Ni2–N1#1	77.80 (10)
N2–Ni1–N3	97.39 (12)	N4#1–Ni2–N1#1	99.79 (12)
O3–Ni1–O5	107.43 (10)	O1#1–Ni2–O1	80.67 (9)
N2–Ni1–O5	94.95 (11)	N4#1–Ni2–O1	106.08 (11)
N3–Ni1–O5	84.54 (11)	N1#1–Ni2–O1	153.09 (10)
O3–Ni1–O1	81.27 (9)	O1#1–Ni2–O3#1	82.02 (9)
N2–Ni1–O1	77.45 (10)	N4#1–Ni2–O3#1	78.09 (11)
N3–Ni1–O1	104.56 (10)	N1#1–Ni2–O3#1	103.94 (10)
O5–Ni1–O1	168.70 (10)	O1–Ni2–O3#1	88.75 (9)
O3–Ni1–Cl1	91.55 (7)	O1#1–Ni2–Cl1	104.54 (7)
N2–Ni1–Cl1	95.09 (9)	N4#1–Ni2–Cl1	96.31 (9)
N3–Ni1–Cl1	166.66 (9)	N1#1–Ni2–Cl1	86.55 (8)
O5–Ni1–Cl1	89.72 (8)	O1–Ni2–Cl1	83.41 (7)
O1–Ni1–Cl1	82.73 (7)	O3#1–Ni2–Cl1	168.74 (7)
Ni1–Cl1–Ni2	88.55 (4)	Ni2–O1–Ni1	104.37 (10)
Ni2#1–O1–Ni2	99.33 (9)	Ni1–O3–Ni2#1	96.82 (10)
Ni2#1–O1–Ni1	95.36 (9)		

[a] Symmetry code: (#1) 2-*x*, 2-*y*, 1-*z*.

Table S2 Selected interatomic distances (Å) and angles (°) for complex **2**.[a]

Ni1···Ni2	3.416	Ni1···Ni2#1	3.094
Ni1···Ni1#1	5.700	Ni2···Ni2#1	3.161
Ni1–O3	2.011 (1)	Ni2–O1#1	2.035 (3)
Ni1–N2	2.052 (4)	Ni2–N4#1	2.051 (5)
Ni1–N3	2.089 (4)	Ni2–N1#1	2.088 (4)
Ni1–O5	2.110 (4)	Ni2–O1	2.104 (3)
Ni1–O1	2.168 (3)	Ni2–O3#1	2.112 (4)
Ni1–Br1	2.5312 (8)	Ni2–Br1	2.5641 (8)
O3–Ni1–N2	156.68 (16)	O1#1–Ni2–N4#1	158.36 (17)
O3–Ni1–N3	78.54 (16)	O1#1–Ni2–N1#1	78.21 (15)
N2–Ni1–N3	99.28 (17)	N4#1–Ni2–N1#1	101.65 (18)
O3–Ni1–O5	108.76 15)	O1#1–Ni2–O1	80.40 (14)
N2–Ni1–O5	93.93 (16)	N4#1–Ni2–O1	104.36 (16)
N3–Ni1–O5	83.80 (16)	N1#1–Ni2–O1	152.91 (15)
O3–Ni1–O1	80.80 (13)	O1#1–Ni2–O3#1	81.63 (13)
N2–Ni1–O1	77.29 (14)	N4#1–Ni2–O3#1	77.43 (17)
N3–Ni1–O1	104.59 (14)	N1#1–Ni2–O3#1	104.25 (15)
O5–Ni1–O1	168.61 (14)	O1–Ni2–O3#1	88.78 (13)
O3–Ni1–Br1	90.70 (10)	O1#1–Ni2–Br1	104.81 (10)
N2–Ni1–Br1	94.88 (12)	N4#1–Ni2–Br1	96.70 (14)
N3–Ni1–Br1	164.70 (13)	N1#1–Ni2–Br1	85.03 (11)
O5–Ni1–Br1	89.51 (11)	O1–Ni2–Br1	84.57 (9)
O1–Ni1–Br1	84.10 (9)	O3#1–Ni2–Br1	169.78 (10)
Ni1–Br1–Ni2	84.19 (2)	Ni2–O1–Ni1	106.19 (14)
Ni2#1–O1–Ni2	99.60 (14)	Ni1–O3–Ni2#1	97.23 (15)
Ni2#1–O1–Ni1	94.76 (13)		

[a] Symmetry code: (#1) -x,1-y,1-z.

Table S3 Selected interatomic distances (Å) and angles (°) for complex **3**.

Ni1···Ni2	2.811	Ni2–N2	1.993(5)
Ni2···Ni3	2.815	Ni2–N7	1.994(4)
Ni3···Ni1	3.187	Ni2–O5	2.328(3)
Ni1–O5	2.042(3)	Ni2–O3	2.413(3)
Ni1–N3	2.042(4)	Ni3–O3	2.033(3)

Ni1–O1	2.049(3)	Ni3–N6	2.038(4)
Ni1–N1	2.061(4)	Ni3–O7	2.054(3)
Ni1–N5	2.070(4)	Ni3–N8	2.072(4)
Ni1–O3	2.110(3)	Ni3–N4	2.076(4)
Ni2–O7	1.938(3)	Ni3–O5	2.133(3)
Ni2–O1	1.942(3)		
O5–Ni1–N3	154.01(14)	N2–Ni2–O5	103.32(14)
O5–Ni1–O1	93.07(12)	N7–Ni2–O5	153.87(15)
N3–Ni1–O1	94.61(14)	O1–Ni2–O3	75.84(12)
O5–Ni1–N1	101.39(14)	O3–Ni2–O5	66.19(10)
N3–Ni1–N1	104.47(16)	O3–Ni2–O7	86.51(12)
O1–Ni1–N1	78.35(13)	O3–Ni2–N2	155.82(15)
O5–Ni1–N5	78.35(13)	O3–Ni2–N7	96.64(15)
N3–Ni1–N5	96.47(16)	O3–Ni3–N6	153.93(15)
O1–Ni1–N5	168.52(14)	O3–Ni3–O7	94.52(13)
N1–Ni1–N5	95.90(15)	N6–Ni3–O7	92.90(15)
O5–Ni1–O3	77.18(12)	O3–Ni3–N8	103.72(14)
N3–Ni1–O3	79.56(14)	N6–Ni3–N8	102.24(16)
O1–Ni1–O3	81.03(12)	O7–Ni3–N8	78.51(14)
N1–Ni1–O3	159.23(13)	O3–Ni3–N4	77.95(13)
N5–Ni1–O3	103.95(14)	N6–Ni3–N4	97.76(16)
O7–Ni2–O1	160.56(13)	O7–Ni3–N4	168.30(14)
O7–Ni2–N2	113.37(16)	N8–Ni3–N4	94.45(15)
O1–Ni2–N2	82.17(15)	O3–Ni3–O5	76.83(11)
O7–Ni2–N7	81.87(15)	N6–Ni3–O5	79.90(15)
O1–Ni2–N7	107.88(15)	O7–Ni3–O5	80.05(12)
N2–Ni2–N7	99.64(17)	N8–Ni3–O5	158.54(14)
O7–Ni2–O5	77.70(12)	N4–Ni3–O5	106.52(13)
O1–Ni2–O5	87.62(11)		

Table S4 Selected interatomic distances (Å) and angles (°) for complex **4**.

Ni1···Ni2	3.204	Ni2–O7	2.062(5)
Ni2···Ni3	2.823	Ni2–N7	2.077(7)
Ni3···Ni1	2.822	Ni2–N6	2.084(7)
Ni1–N5	2.038(7)	Ni2–O1	2.149(5)
Ni1–O1	2.042(5)	Ni3–O7	1.946(6)
Ni1–O3	2.049(5)	Ni3–O3	1.954(5)
Ni1–N3	2.078(6)	Ni3–N4	1.998(7)
Ni1–N1	2.083(6)	Ni3–N8	2.014(7)
Ni1–O5	2.126(5)	Ni3–O5	2.420(5)
Ni2–O5	2.034(5)	Ni3–O1	2.319(5)
Ni2–N2	2.047(7)		
N5–Ni1–O1	154.3(2)	O7–Ni2–N6	168.2(2)
N5–Ni1–O3	94.4(2)	N7–Ni2–N6	94.3(3)
O1–Ni1–O3	92.7(2)	O5–Ni2–O1	76.51(19)
N5–Ni1–N3	104.3(3)	N2–Ni2–O1	80.9(3)
O1–Ni1–N3	101.4(2)	O7–Ni2–O1	79.8(2)
O3–Ni1–N3	78.4(2)	N7–Ni2–O1	158.2(2)
N5–Ni1–N1	97.1(3)	N6–Ni2–O1	106.9(2)
O1–Ni1–N1	78.2(2)	O7–Ni3–O3	160.5(2)
O3–Ni1–N1	168.1(2)	O7–Ni3–N4	113.1(3)
N3–Ni1–N1	95.7(3)	O3–Ni3–N4	82.5(3)
N5–Ni1–O5	79.9(2)	O7–Ni3–N8	81.8(3)
O1–Ni1–O5	76.9(2)	O3–Ni3–N8	107.8(3)
O3–Ni1–O5	81.00(19)	N4–Ni3–N8	100.0(3)
N3–Ni1–O5	159.2(2)	O7–Ni3–O1	78.1(2)
N1–Ni1–O5	104.0(2)	O3–Ni3–O1	87.29(19)
O5–Ni2–N2	154.4(3)	N4–Ni3–O1	102.8(2)
O5–Ni2–O7	94.6(2)	N8–Ni3–O1	154.1(2)
N2–Ni2–O7	93.0(3)	O1–Ni3–O5	66.30(16)
O5–Ni2–N7	103.9(2)	O3–Ni3–O5	75.83(18)
N2–Ni2–N7	101.5(3)	O5–Ni3–O7	86.43(19)
O7–Ni2–N7	78.4(2)	O5–Ni3–N4	156.0(2)
O5–Ni2–N6	77.9(2)	O5–Ni3–N8	96.4(3)
N2–Ni2–N6	97.7(3)		

Table S5 Selected interatomic distances (Å) and angles (°) for complex **5**.[a]

Ni1···Ni#1	3.176	Ni3···Ni3#2	3.172
Ni1···Ni2	2.849	Ni3···Ni4	2.844
Ni1–N3	2.048(3)	Ni3–O5	2.064(2)
Ni1–O3#1	2.051(2)	Ni3–N5	2.082(3)
Ni1–O1	2.067(2)	Ni3–N8#2	2.089(3)
Ni1–N1	2.093(3)	Ni3–O7	2.135(2)
Ni1–N4#1	2.093(3)	Ni4—O7	2.433(3)
Ni1–O3	2.107(2)	Ni4—O7#2	2.433(3)
Ni2–O1#1	1.931(3)	Ni4–O5#2	1.942(2)
Ni2–O1	1.931(3)	Ni4–O5	1.942(2)
Ni2–N2	2.002(4)	Ni4–N6#2	1.997(3)
Ni2–N2#1	2.002(4)	Ni4–N6	1.997(3)
Ni2—O3	2.436(2)	O3–Ni1#1	2.051(2)
Ni2—O3#1	2.436(2)	O7–Ni3#2	2.037(2)
Ni3–N7	2.031(3)	N4–Ni1#1	2.093(3)
Ni3–O7#2	2.037(2)	N8–Ni3#2	2.089(3)
N3–Ni1–O3#1	154.03(11)	N7–Ni3–O7#2	154.80(11)
N3–Ni1–O1	96.71(12)	N7–Ni3–O5	95.16(11)
O3#1–Ni1–O1	93.24(10)	O7#2–Ni3–O5	93.39(10)
N3–Ni1–N1	101.13(12)	N7–Ni3–N5	101.17(12)
O3#1–Ni1–N1	104.38(11)	O7#2–Ni3–N5	103.76(11)
O1–Ni1–N1	78.08(11)	O5–Ni3–N5	78.40(11)
N3–Ni1–N4#1	96.12(13)	N7–Ni3–N8#2	96.81(13)
O3#1–Ni1–N4#1	77.52(11)	O7#2–Ni3–N8#2	78.03(11)
O1–Ni1–N4#1	165.93(12)	O5–Ni3–N8#2	166.79(11)
N1–Ni1–N4#1	93.79(12)	N5–Ni3–N8#2	93.76(12)
N3–Ni1–O3	79.82(11)	N7–Ni3–O7	79.34(11)
O3#1–Ni1–O3	77.84(10)	O7#2–Ni3–O7	78.36(10)
O1–Ni1–O3	82.26(9)	O5–Ni3–O7	82.39(9)
N1–Ni1–O3	160.30(11)	N5–Ni3–O7	160.76(11)
N4#1–Ni1–O3	105.73(11)	N8#2–Ni3–O7	105.32(11)
O1#1–Ni2–O1	159.49(15)	O5#2–Ni4–O5	159.54(15)
O1#1–Ni2–N2	109.81(13)	O5#2–Ni4–N6#2	82.56(12)
O1–Ni2–N2	82.86(12)	O5–Ni4–N6#2	109.89(12)
O1#1–Ni2–N2#1	82.86(12)	O5#2–Ni4–N6	109.89(12)
O1–Ni2–N2#1	109.81(13)	O5–Ni4–N6	82.56(12)
N2–Ni2–N2#1	105.90(19)	N6#2–Ni4–N6	107.18(19)
O3–Ni2–O1	76.97(9)	O7–Ni4–O5	77.55(9)
O3–Ni2–O1#1	85.71(10)	O7–Ni4–O5#2	85.25(9)
O3–Ni2–O3#1	64.86(8)	O7–Ni4–O7#2	65.62(8)
O3–Ni2–N2	153.55(11)	O7–Ni4–N6	153.64(11)
O3–Ni2–N2#1	97.00(11)	O7–Ni4–N6#2	95.85(11)
O3#1–Ni2–O1	85.71(10)	O7#2–Ni4–O5	85.25(9)
O3#1–Ni2–O1#1	76.97(9)	O7#2–Ni4–O5#2	77.55(9)
O3#1–Ni2–N2	97.00(11)	O7#2–Ni4–N6	95.85(11)
O3#1–Ni2–N2#1	153.55(11)	O7#2–Ni4–N6#2	153.64(11)

[a] Symmetry codes: (#1) 1-x,y,1/2-z, (#2) 2-x,y,1/2-z.

Table S6 The refcodes of the 24 planar tetranuclear Ni^{II} complexes comprising the $[Ni_4X_6]$ core (X = donor atom).

BIFKEH	HOWQUF	LOMSUC	UKISOW
BIFKIL	IGOJUJ	RICQAW	UKISUC
CUFTUS	JAZROS	SAXNUB	MOTMOY
DEGSAK	KAMNES	SEKPEE	IGIGAH
FIQKUM	KISBAQ	TIVSIB	RUMYII
FIQLIB	KISBEU	TIVSOH	RUMYII01