

Electronic Supplementary Information

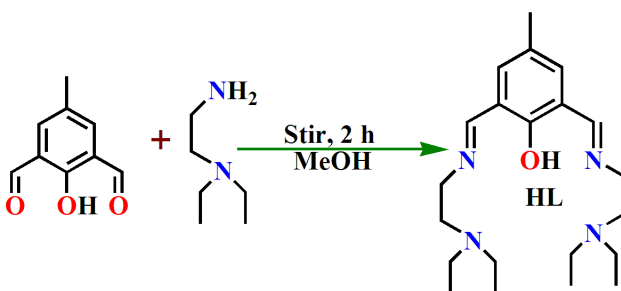
Dinuclear Nickel Complexes of Divergent Ni...Ni Separation Showing Ancillary Ligand Addition and Bio-macromolecular Interaction

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Scheme S1. Synthetic procedure of the ligand HL

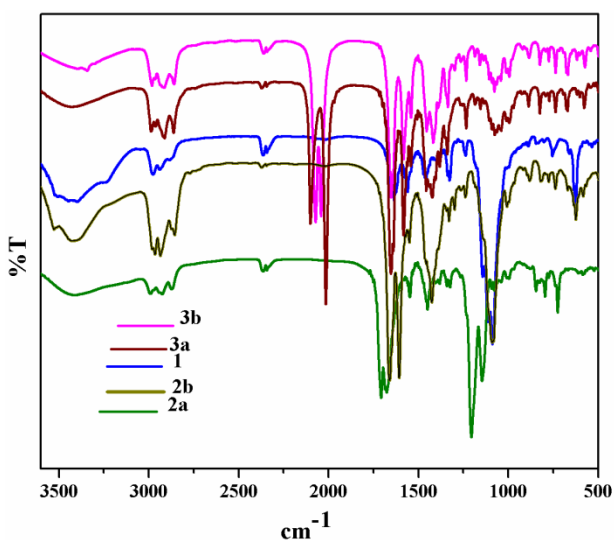


Fig. S1. FT-IR spectra of **1-3b**.

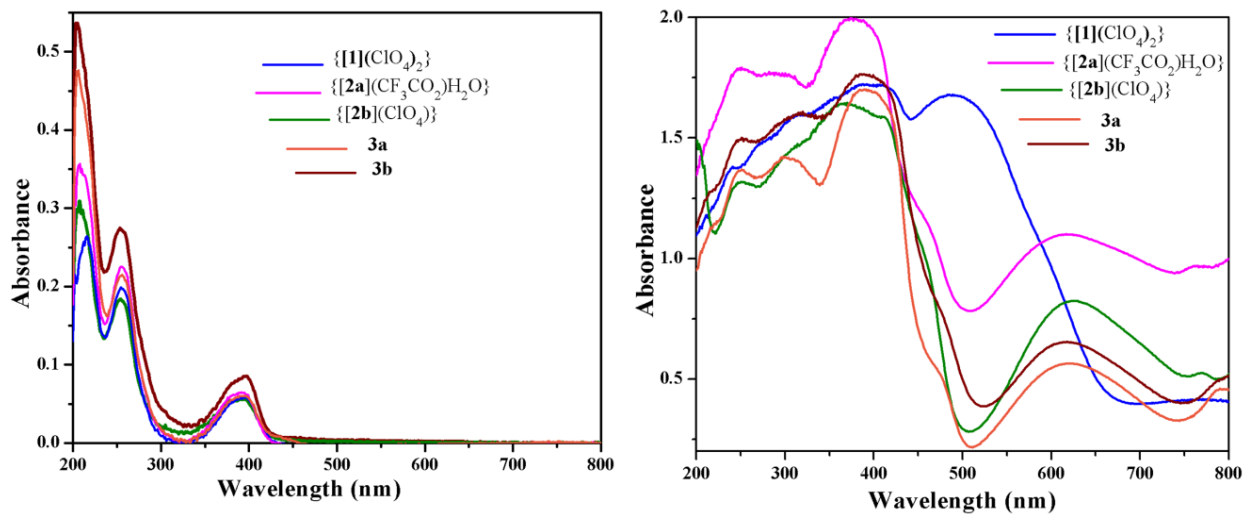


Fig. S2. UV-vis spectra of five complexes in MeOH (left) and in solid state (right).

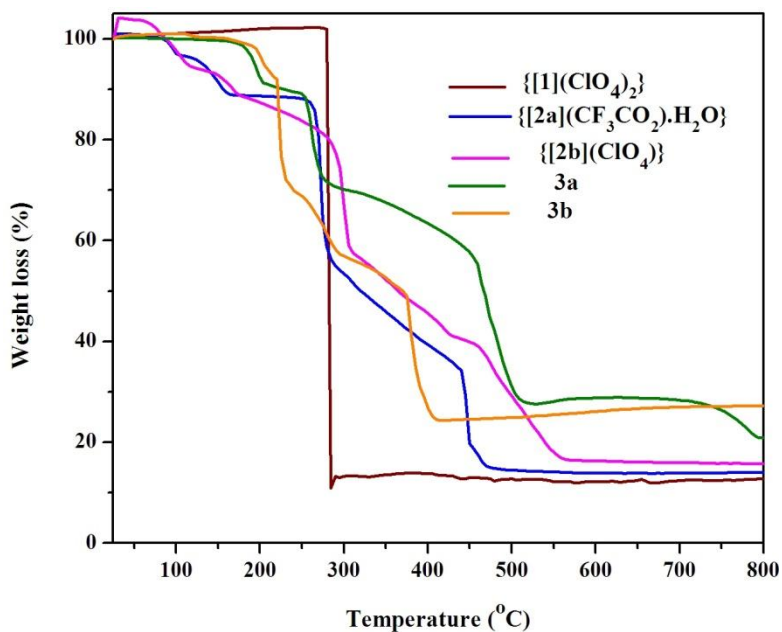


Fig. S3. TGA curves for **1-3b** up to 800 °C.

Table S1. Selected bond lengths (Å) and bond angles (°) of $1(ClO_4)_2$

$1(ClO_4)_2$
Distances

Ni1–N1	1.881(8)	Ni2–O1	1.914(6)
Ni1–O2	1.913(7)	Ni2–N3	1.831(8)
Ni1–O1	1.858(6)	Ni2–O2	1.859(7)
Ni1–N2	1.911(8)	Ni2–N4	1.984(8)
Angles			
N1–Ni1–O2	174.4(3)	N3–Ni2–O2	173.2(3)
N1–Ni1–O1	94.8(3)	N3–Ni2–O1	93.6(3)
O2–Ni1–O1	79.7(3)	O2–Ni2–O1	79.6(3)
N1–Ni1–N2	87.3(3)	N3–Ni2–N4	88.6(3)
O2–Ni1–N2	98.2(3)	O2–Ni2–N4	98.2(3)
O1–Ni1–N2	177.8(3)	O1–Ni2–N4	177.4(3)
Ni1–O1–Ni2	100.3(3)	Ni2–O2–Ni1	100.3(3)

Table S2. Hydrogen bonding interaction in **1**

D–H···A	D–H (Å)	D···A (Å)	H···A (Å)	< (D–H···A) (°)
O(2)–H(2)···O(13)	0.88(12)	3.072(12)	2.29(11)	147(10)

Table S3 Selected bond lengths (Å) and bond angles (°) of **2a**(CF₃CO₂)·H₂O and **2b**(ClO₄)·C₃H₇NO

[2a (CF ₃ CO ₂)·H ₂ O]			
Distances			
Ni1–N3A	1.982(3)	Ni2–N1A	1.982(3)
Ni1–O3A	2.002(2)	Ni2–O6A	2.025(3)
Ni1–O1A	2.048(2)	Ni2–O4A	2.066(3)
Ni1–O5A	2.090(3)	Ni2–O1A	2.078(2)
Ni1–O2A	2.110(3)	Ni2–O7A	2.123(3)
Ni1–N4A	2.213(3)	Ni2–N2A	2.212(3)
Angles			
N3A–Ni1–O3A	172.35(12)	N1A–Ni2–O6A	172.60(13)

N3A-Ni1-O1A	89.44(11)	N1A-Ni2-O4A	94.31(13)
O3A-Ni1-O1A	96.62(10)	O6A-Ni2-O4A	90.94(13)
N3A-Ni1-O5A	90.50(12)	N1A-Ni2-O1A	87.89(11)
O3A-Ni1-O5A	94.22(12)	O6A-Ni2-O1A	97.14(10)
O1A-Ni1-O5A	89.32(10)	O4A-Ni2-O1A	91.98(10)
N3A-Ni1-O2A	87.50(12)	N1A-Ni2-O7A	88.16(13)
O3A-Ni1-O2A	88.05(12)	O6A-Ni2-O7A	86.66(13)
O1A-Ni1-O2A	87.99(11)	O4A-Ni2-O7A	177.40(13)
O5A-Ni1-O2A	176.66(12)	O1A-Ni2-O7A	87.34(11)
N3A-Ni1-N4A	83.27(12)	N1A-Ni2-N2A	81.62(14)
O3A-Ni1-N4A	90.69(11)	O6A-Ni2-N2A	93.43(13)
O1A-Ni1-N4A	172.69(10)	O4A-Ni2-N2A	87.52(13)
O5A-Ni1-N4A	90.10(11)	O1A-Ni2-N2A	169.43(12)
O2A-Ni1-N4A	92.31(12)	O7A-Ni2-N2A	93.62(14)
[2b(ClO₄)·C₃H₇NO]			
Distances			
Ni1-N1	1.992(2)	Ni2-N3	2.010(2)
Ni1-O5	2.042(2)	Ni2-O4	2.033(2)
Ni1-O3	1.997(2)	Ni2-O6	2.027(2)
Ni1-O1	2.050(2)	Ni2-O1	2.050(2)
Ni1-O7	2.138(2)	Ni2-O2	2.150(2)
Ni1-N2	2.250(2)	Ni2-N4	2.214(2)
Angles			
N1-Ni1-O5	88.60(9)	N3-Ni2-O4	92.20(8)
N1-Ni1-O3	172.52(9)	N3-Ni2-O6	170.14(9)
O3-Ni1-O5	97.72(8)	O6-Ni2-O4	93.04(7)
N1-Ni1-O1	87.67(7)	N3-Ni2-O1	88.27(8)
O5-Ni1-O1	91.80(7)	O4-Ni2-O1	91.63(7)
O3-Ni1-O1	96.07(7)	O6-Ni2-O1	99.92(7)
N1-Ni1-O7	88.36(8)	N3-Ni2-O2	89.94(8)

O5-Ni1-O7	176.28(7)	O4-Ni2-O2	177.52(7)
O3-Ni1-O7	85.17(7)	O6-Ni2-O2	85.03(7)
O1-Ni1-O7	90.23(7)	O1-Ni2-O2	87.17(7)
N1-Ni1-N2	82.46(8)	N3-Ni2-N4	82.00(9)
O5-Ni1-N2	88.44(8)	O4-Ni2-N4	87.80(8)
O1-Ni1-N2	170.12(7)	O6-Ni2-N4	89.86(8)
O7-Ni1-N2	89.03(8)	O1-Ni2-N4	170.22(7)
O3-Ni1-N2	93.68(7)	O2-Ni2-N4	93.75(8)

Table S4. Hydrogen bonding interactions in **2a** and **2b**

D—H···A	D—H (Å)	D···A (Å)	H···A (Å)	< (D—H···A) (°)
2a				
O(2A)-H(22)···O(8A)	0.858	2.811	1.967	173.80
O(2A)-H(21)···O(10A)	0.741	2.738	2.035	158.65
O(10A)-H(102)···O(9A)*	1.000	2.858	1.907	157.98
O(10A)-H(101)···O(9A)	1.013	2.865	1.972	165.96
2b				
O(7)-H(7X)···O(9)	0.85	2.903	2.14	148
O(7)-H(7Y)···O(8)	0.85	2.674	1.83	170

D, donor; A, acceptor; H, hydrogen

Table S5. Selected bond lengths (Å) and bond angles (°) of **3a** and **3b**

3a			
Distances			
Ni1-N1	2.003(10)	Ni2-N5	1.990(9)
Ni1-N3	2.045(11)	Ni2-O3	2.029(8)
Ni1-O1	2.047(7)	Ni2-O1	2.025(8)
Ni1-O2	2.041(8)	Ni2-O4	2.126(11)
Ni1-N4	2.150(10)	Ni2-N4	2.108(10)
Ni1-N2	2.209(9)	Ni2-N6	2.161(11)

Angles			
N1-Ni1-N3	91.5(4)	N5-Ni2-O3	91.6(4)
N1-Ni1-O1	89.5(4)	N5-Ni2-O1	88.8(4)
N3-Ni1-O1	91.6(4)	O1-Ni2-O3	89.2(3)
N1-Ni1-O2	87.0(3)	N5-Ni2-O4	85.1(5)
N3-Ni1-O2	178.3(5)	O3-Ni2-O4	176.7(4)
O2-Ni1-O1	87.5(3)	O1-Ni2-O4	90.8(4)
N1-Ni1-N4	170.4(4)	N5-Ni2-N4	170.4(5)
N3-Ni1-N4	90.1(4)	O3-Ni2-N4	92.3(3)
O1-Ni1-N4	81.0(3)	O1-Ni2-N4	82.5(3)
O2-Ni1-N4	91.3(3)	N4-Ni2-O4	90.9(4)
N1-Ni1-N2	83.5(4)	N5-Ni2-N6	83.5(4)
N3-Ni1-N2	90.4(4)	O3-Ni2-N6	93.0(4)
O1-Ni1-N2	172.7(3)	O1-Ni2-N6	172.0(4)
O2-Ni1-N2	90.3(4)	O4-Ni2-N6	86.6(5)
N4-Ni1-N2	106.0(4)	N4-Ni2-N6	105.0(4)
3b			
Distances			
Ni1-N1	1.996(4)	Ni2-N3	1.991(4)
Ni1-O2	2.037(3)	Ni2-O1	2.052(3)
Ni1-O1	2.042(3)	Ni2-O3	2.074(3)
Ni1-N5	2.095(3)	Ni2-N5	2.096(3)
Ni1-O4	2.128(3)	Ni2-N8	2.126(4)
Ni1-N2	2.202(4)	Ni2-N4	2.199(4)
Angles			
N1-Ni1-O2	92.17(15)	N3-Ni2-O1	89.38(13)
N1-Ni1-O1	89.11(13)	N3-Ni2-O3	91.56(14)

O2-Ni1-O1	89.99(12)	O1-Ni2-O3	88.79(12)
N1-Ni1-N5	172.25(15)	N3-Ni2-N5	172.58(14)
O2-Ni1-N5	90.39(13)	O1-Ni2-N5	83.25(12)
O1-Ni1-N5	83.57(12)	O3-Ni2-N5	89.03(13)
N1-Ni1-O4	88.49(14)	N3-Ni2-N8	89.01(15)
O2-Ni1-O4	177.73(13)	O1-Ni2-N8	91.41(13)
O1-Ni1-O4	92.19(11)	O3-Ni2-N8	179.40(14)
N5-Ni1-O4	89.23(13)	N5-Ni2-N8	90.43(14)
N1-Ni1-N2	83.41(15)	N3-Ni2-N4	83.51(15)
O2-Ni1-N2	90.24(14)	O1-Ni2-N4	172.87(13)
O1-Ni1-N2	172.53(13)	O3-Ni2-N4	90.95(14)
N5-Ni1-N2	103.90(14)	N5-Ni2-N4	103.87(14)
O4-Ni1-N2	87.68(13)	N8-Ni2-N4	88.93(15)
Ni1-O1-Ni2	95.77(11)	Ni1-N5-Ni2	92.96(14)

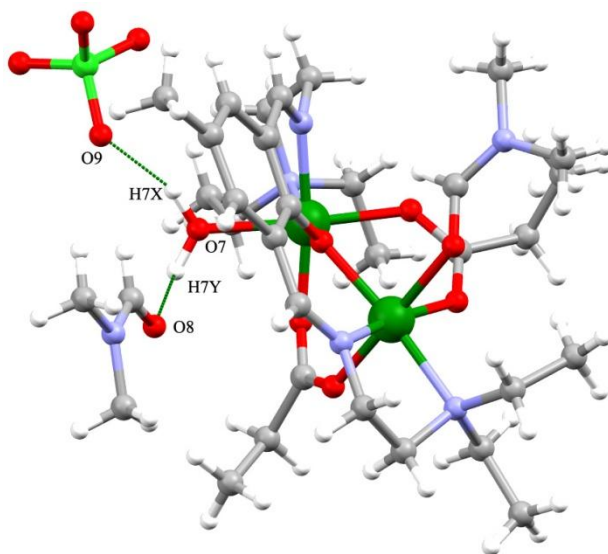


Fig. S4. View of intramolecular hydrogen-bonding for trapping of anions and solvents in the crystal lattice in **2b**.

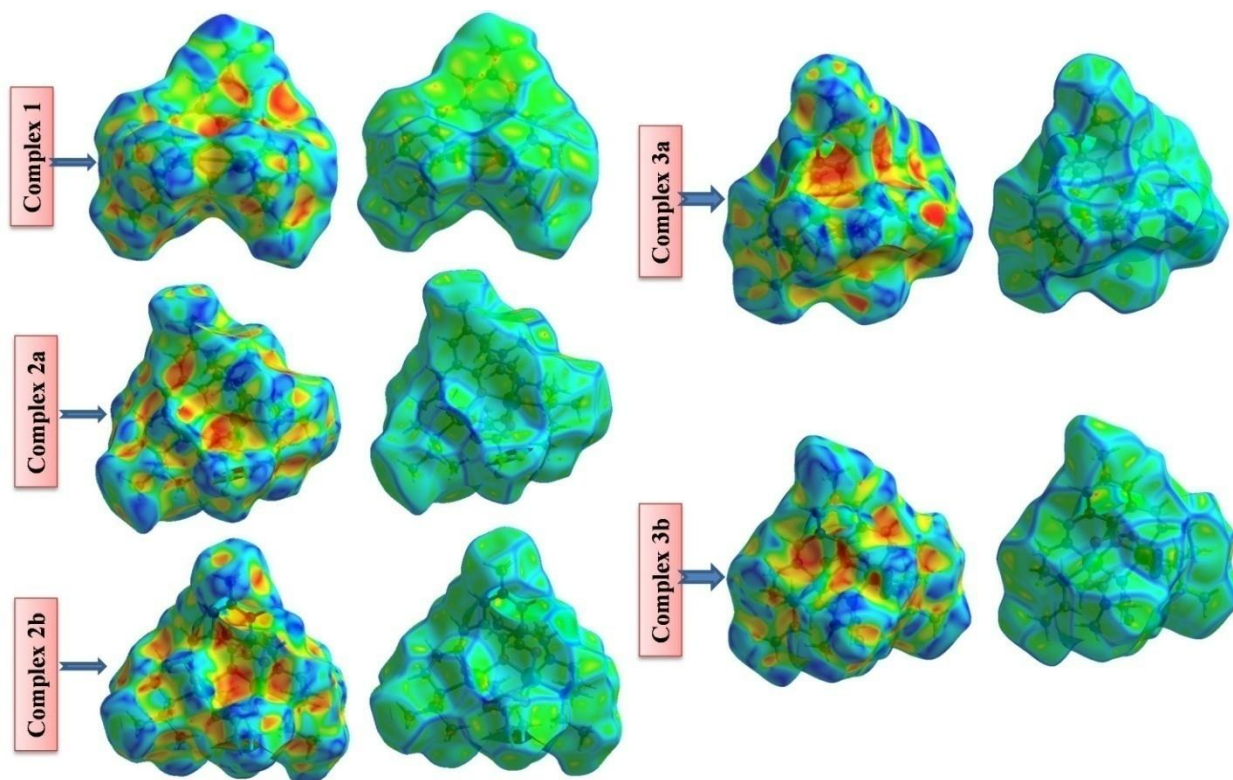


Fig. S5. Hirshfeld surfaces of **1-3b** mapped over shape index (left) and curvedness (right).