Supplementary Information to the Paper

2,6-Dipicolinoylbis(N,N-dialkylthioureas) as Versatile Building Blocks for Oligo- and Polynuclear Architectures

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1. X-Ray structure determinations

Fig. S1: Ellipsoid plot of $[Ni_2(L^a)_2(MeOH)(H_2O)]$ (**5**)
Table S1: Selected bond lengths and angles of $[Ni_2(L^a)_2(MeOH)(H_2O)]$ (**5**)

Fig. S2: Ellipsoid plot of $[Ni_2Pr(L^a)_2(OAc)_3(MeOH)_2]$
Table S2: Selected bond lengths and angles in $[Ni_2Pr(L^a)_2(OAc)_3(MeOH)_2]$

Fig. S3: Ellipsoid plot of $[Ni_2Ba(L^a)_3]$
Table S3: Selected bond lengths and angles in $[Ni_2Ba(L^a)_3]$

Fig. S4: Ellipsoid plot of $\{[Cu_2Dy(L^a)_2(p-O_2C-C_6H_4-CO_2)]Cl\}$
Table S4: Selected bond lengths and angles in $\{[Cu_2Dy(L^a)_2(p-O_2C-C_6H_4-CO_2)]Cl\}$

Fig. S5: Ellipsoid plot of $[Mn_2Ba(MeOH)(L^b)_3]_\infty$
Table S5: Selected bond lengths and angles in $[Mn_2Ba(MeOH)(L^b)_3]_\infty$

2. Computational Calculations

Fig. S6: Optimized structure of compound **5**
Table S6: Structural optimization of **5** and comparison with experimental data

Fig. S1: Ellipsoid plot of [Ni$_2$(L^a)$_2$(MeOH)(H$_2$O)] (**5**)
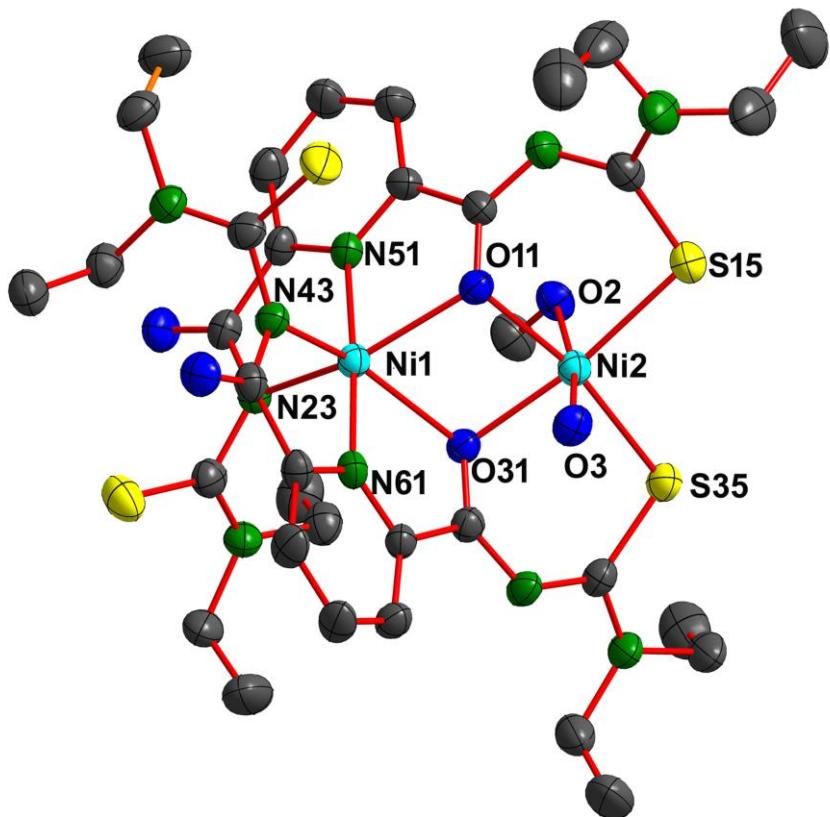
Table S1: Selected bond lengths and angles of [Ni$_2$(L^a)$_2$(MeOH)(H$_2$O)] (**5**)

Bond lengths (Å)			
Ni1–O11	2.193(3)	Ni2–O11	2.081(3)
Ni1–O31	2.229(3)	Ni2–O31	2.075(3)
Ni1–N23	2.086(4)	Ni2–S15	2.381(1)
Ni1–N43	2.085(3)	Ni2–S35	2.362(1)
Ni1–N51	1.989(3)	Ni2–O2	2.145(3)
Ni1–N61	1.992(3)	Ni2–O3	2.109(3)
Angles (°)			
O11-Ni1-N23	150.0(1)	O11-Ni2-S35	168.8(1)
O31- Ni1-N43	150.6(1)	O31- Ni2-S15	172.1(1)
N51- Ni1-N61	176.4(1)	O2- Ni2-O3	170.5(1)

Fig. S2: Ellipsoid plot of [Ni$_2$Pr(L^a)$_2$(OAc)$_3$(MeOH)$_2$]
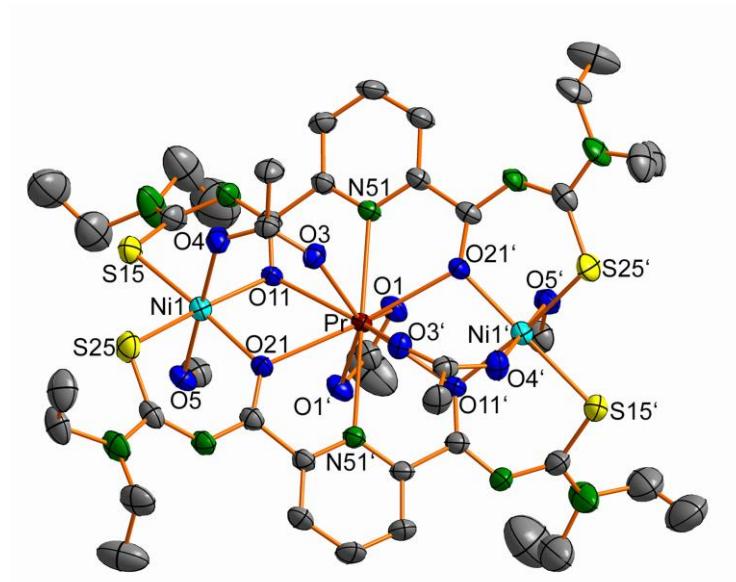
Table S2: Selected bond lengths and angles in [Ni$_2$Pr(L^a)$_2$(OAc)$_3$(MeOH)$_2$]

Bond lengths (Å)			
Pr-O1/ O1$^{(1)}$	2.592(2)	Ni1–O5	2.143(2)
Pr -O3/O3$^{(1)}$	2.437(2)	Ni1–O11	2.084(2)
Pr -N51/N51$^{(1)}$	2.643(2)	Ni1–O21$^{(1)}$	2.045(2)
Pr -O11/O11$^{(1)}$	2.580(2)	Ni1–S15	2.387(1)
Pr -O21/O21$^{(1)}$	2.537(2)	Ni1– S25$^{(1)}$	2.339(1)
Ni1–O4	2.069(2)		
Angles (°)			
O11-Ni1-S25$^{(1)}$	173.12(6)	N51-Ln-N51$^{(1)}$	174.71(10)
S15- Ni1-O21$^{(1)}$	171.27(6)	O11-Ln-O11$^{(1)}$	143.83(8)
O5- Ni1-O4	178.57(8)	O21-Ln-O21$^{(1)}$	157.92(9)

Symmetry codes: $^{(1)}$ –x, y, 1/2 –z.

Fig. S3: Ellipsoid plot of [Ni$_2$Ba(L^a)$_3$]
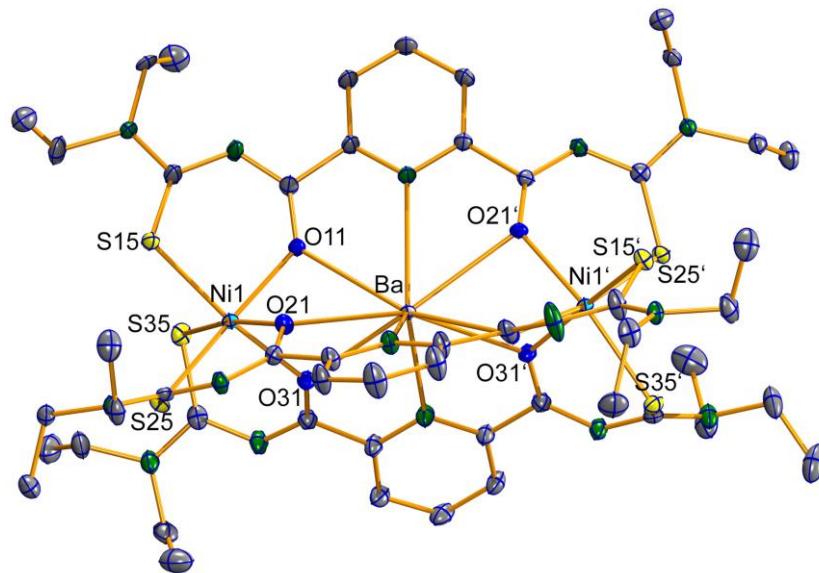
Table S3: Selected bond lengths and angles in [Ni$_2$Ba(L^a)$_3$]

Bond lengths (Å)			
Ba1-O11/ O11[(1)]	2.776(1)	Ni1–O11	2.072(1)
Ba1-O21/O21[(1)]	2.821(1)	Ni1–S15	2.381(1)
Ba1-O31/O31[(1)]	2.750(1)	Ni1–O21[(1)]	2.077(1)
Ba1-N51/N51[(1)]	2.893(2)	Ni1–S25[(1)]	2.381(1)
Ba1-N61	2.928(3)	Ni1–O31	2.076(1)
Ba1-Ni1/Ni1[(1)]	3.658(1)	Ni1– S35	2.457(1)
Angles (°)			
O31-Ni1-S15	172.12(5)	O5- Ni1-O4	168.71(5)
O11- Ni1-S25[(1)]	169.97(4)	Ni1-Ba-Ni1[(1)]	179.046(10)

Fig. S4: Ellipsoid plot of $[Cu_2Dy(L^a)_2(p-O_2C-C_6H_4-CO_2)]^+$
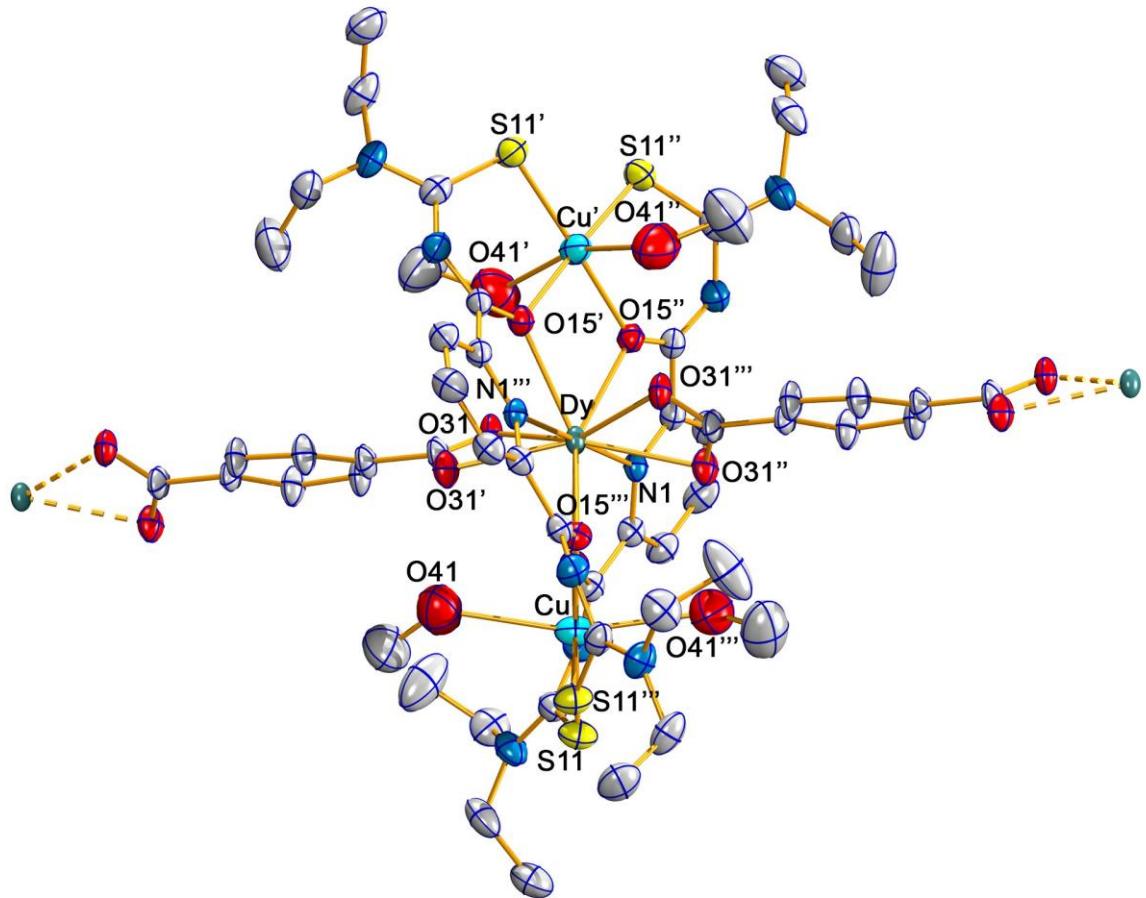
Table S4: Selected bond lengths in $[Cu_2Dy(L^a)_2(p-O_2C-C_6H_4-CO_2)]^+$

Bond lengths (Å)			
Cu-S11	2.776(1)	Cu-O41	2.072(1)
Cu-O15	1.989(4)	Dy-O15	2.462(4)
Dy-N1	2.246(2)	Dy–O31	2.463(4)

Fig. S5: Ellipsoid plot of [Mn$_2$Ba(MeOH)(L^b)$_3$]
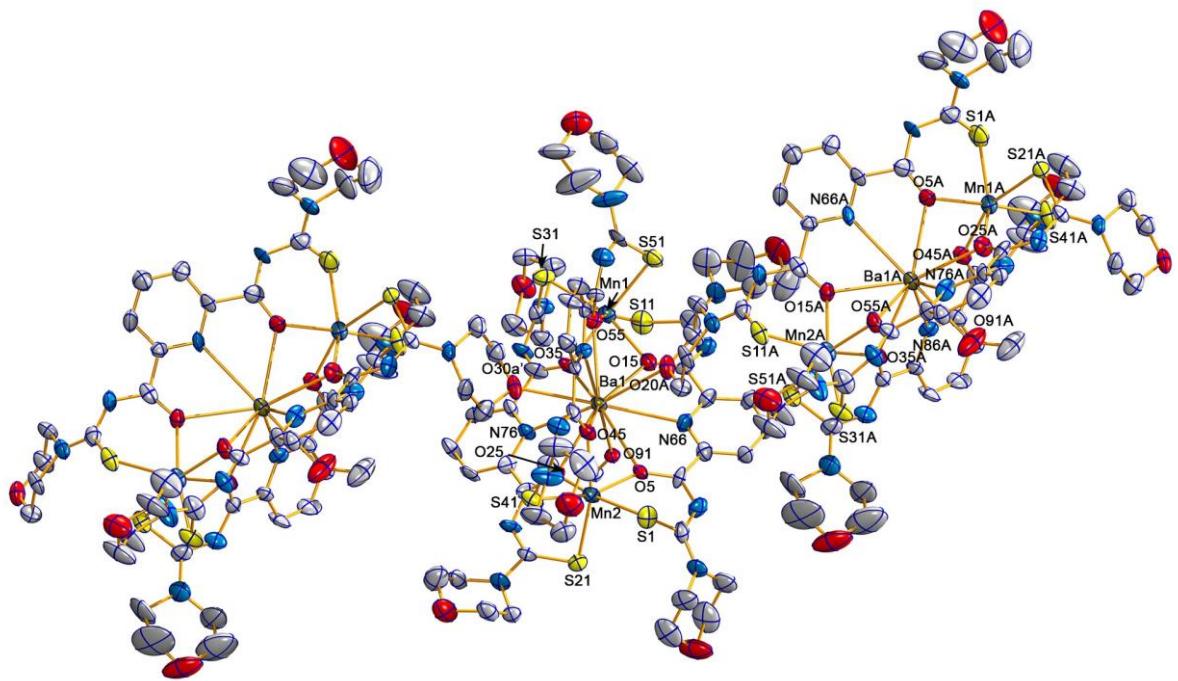
Table S5: Selected bond lengths in [Mn$_2$Ba(MeOH)(L^b)$_3$]

Bond lengths (Å)			
Mn1-O15/O35/O55	2.155(9)/2.145(9)/2.182(9)	Ba1–O15/O35/O55	2.2.79(1)/2.775(8)/2.810(9)
Mn1-S11/S31/S51	2.604(5)/2.579(4)/2.539(5)	Ba1–N66/N76/N86	2.2.98(1)/3.02(1)/2.98(1)
Mn2-O5/O25/O45	2.2.146(9)/2.151(9)/2.152(9)	Ba1–O20A/O30a'/O91	3.09(1)/3.021(9)/3.02(2)
Mn2-S1/S21/S41	2.555(4)/2.549(5)/2.554(4)	Ba1A-O5A/O25A/O45A	2.837(9)/2.752(9)/2.78(1)
Mn1A-O5A/O25A/O45A	2.147(9)/2.17(1)/2.23(1)	Ba1A-N66A/N76A/N86A	3.04(1)/2.90(1)/2.90(1)
Mn1A-S1A/S21A/S41A	2.566(5)/2.620(4)/2.523(4)	Ba1A-O91A	2.87(1)
Mn2A-O15A/O35A/O55A	2.17(1)/2.201(9)/2.16(1)		
Mn2A-S11A/S31A/S51A	2.585(5)/2.564(5)/2.571(5)		

Fig. S6: Optimized structure of **5**. Hydrogen atoms bonded to carbon atoms are omitted for clarity.
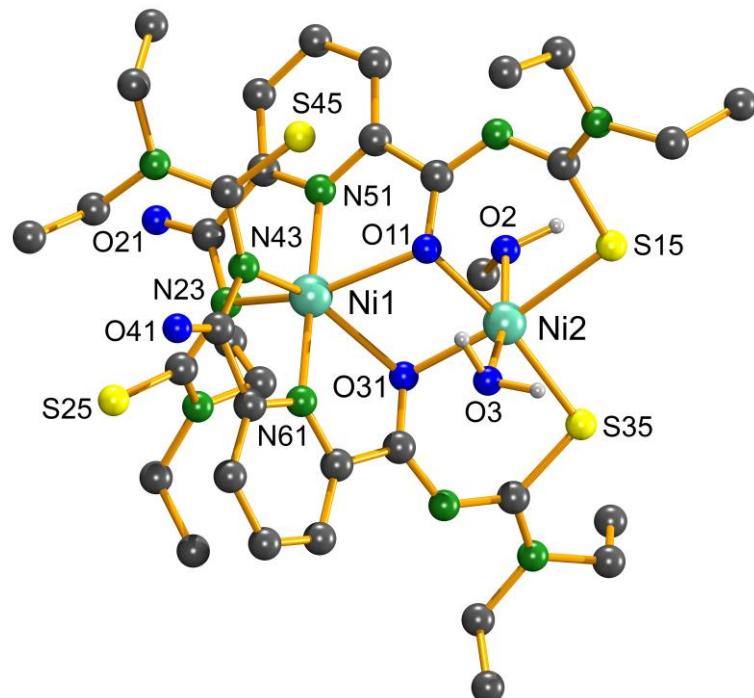

Table S6: Comparison between experimental and calculated data

Bond lengths (Å)		
Bonds	Experimental	Calculated*
Ni1–O11	2.193(3)	2.239(3)
Ni1–O31	2.229(3)	2.321(3)
Ni1–N23	2.086(4)	2.086(3)
Ni1–N43	2.085(3)	2.052(4)
Ni1–N51	1.989(3)	2.003(8)
Ni1–N61	1.992(3)	2.006(4)
Ni2–O11	2.081(3)	2.069(9)
Ni2–O31	2.075(3)	2.071(6)
Ni2–S15	2.381(1)	2.416(4)
Ni2–S35	2.362(1)	2.376(8)
Ni2–O2	2.145(3)	2.105(2)
Ni2–O3	2.109(3)	2.117(1)
Angles (°)		
Angels	Experimental	Calculated*
O11-Ni1-N23	150.0(1)	147.5(4)
O31- Ni1-N43	150.6(1)	149.1(3)
N51- Ni1-N61	176.4(1)	179.3(7)
O11-Ni2-S35	168.8(1)	171.1(2)
O31- Ni2-S15	172.1(1)	172.1(4)
O2- Ni2-O3	170.5(1)	168.6(4)

* DFT calculation with PBE1PBE exchange correlation functional with the basis sets LanL2TZ/ 6-311G*/ 6-311G for Ni/ C, O, N, S/ H atoms, respectively.