Supplementary Information

Zn/Ni and Zn/Pd Heterobimetallic Coordination Polymers with $[SSC\text{-}N(CH_2COO)_2]^{3-}$ Ligands

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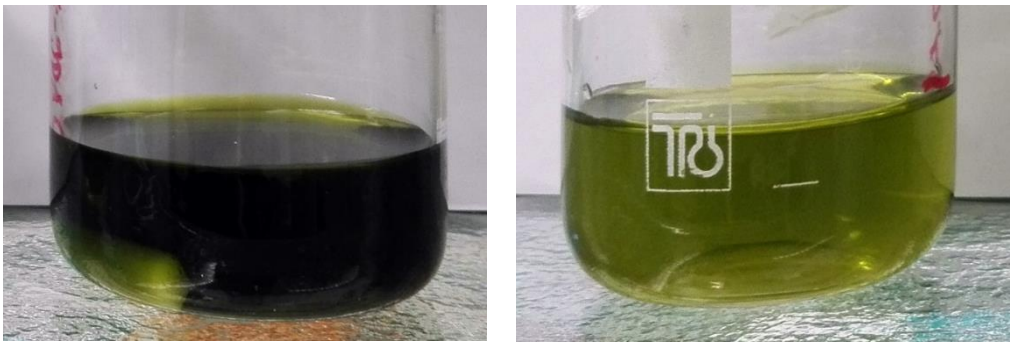
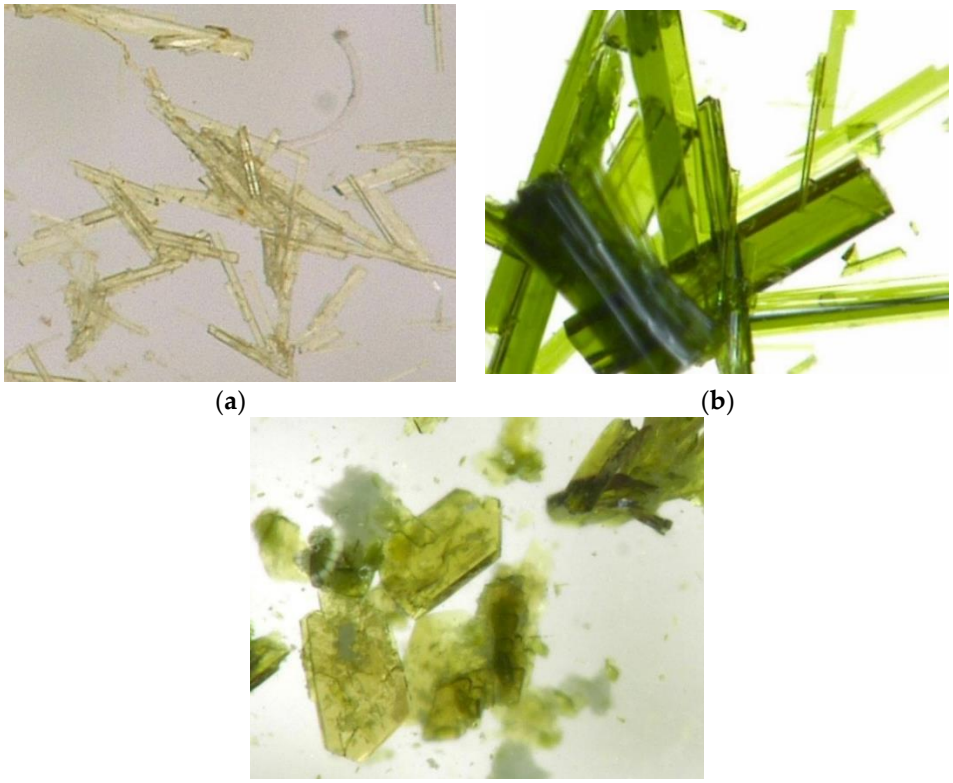


(**a**) (**b**)

Figure S1. Reaction solutions of $[Ni(H_2L)_2]$ (**2-Ni**) with 4 Equiv. $Zn(OAc)_2$ in water: (**a**) stirred at room temperature, and (**b**) stirred at 80 °C.



(**a**) (**b**)

(**c**)

Figure S2. Single crystals of heterobimetallic coordination polymers (photographic images at 200-fold magnification): (**a**) $Zn_2[Pd(L)_2]$ (**4-Pd**) · $14H_2O$, (**b**) $Zn_2[Ni(L)_2]$ (**4-Ni**) · $14H_2O$, and (**c**) $Zn_2[Ni(L)_2]$ (**5-Ni**) · 2.5 acetone · 8.5 H_2O.

NMR and IR spectra

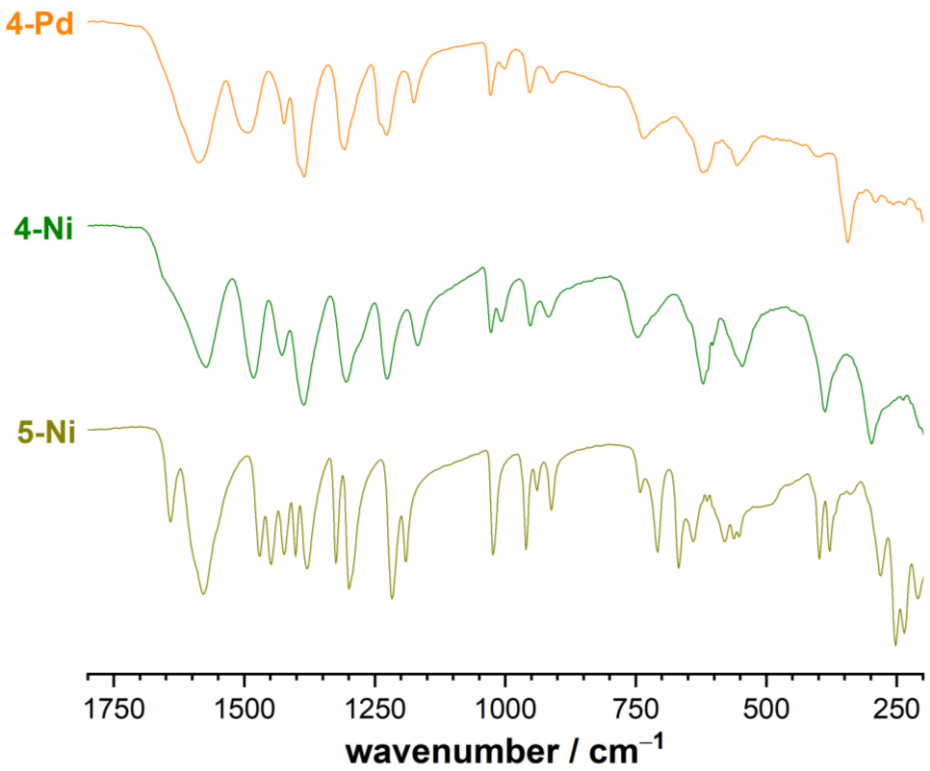


Figure S3. ATR-IR spectra of **4-Pd** · 12H_2O, **4-Ni** · 2H_2O, and **5-Ni** · 2H_2O.

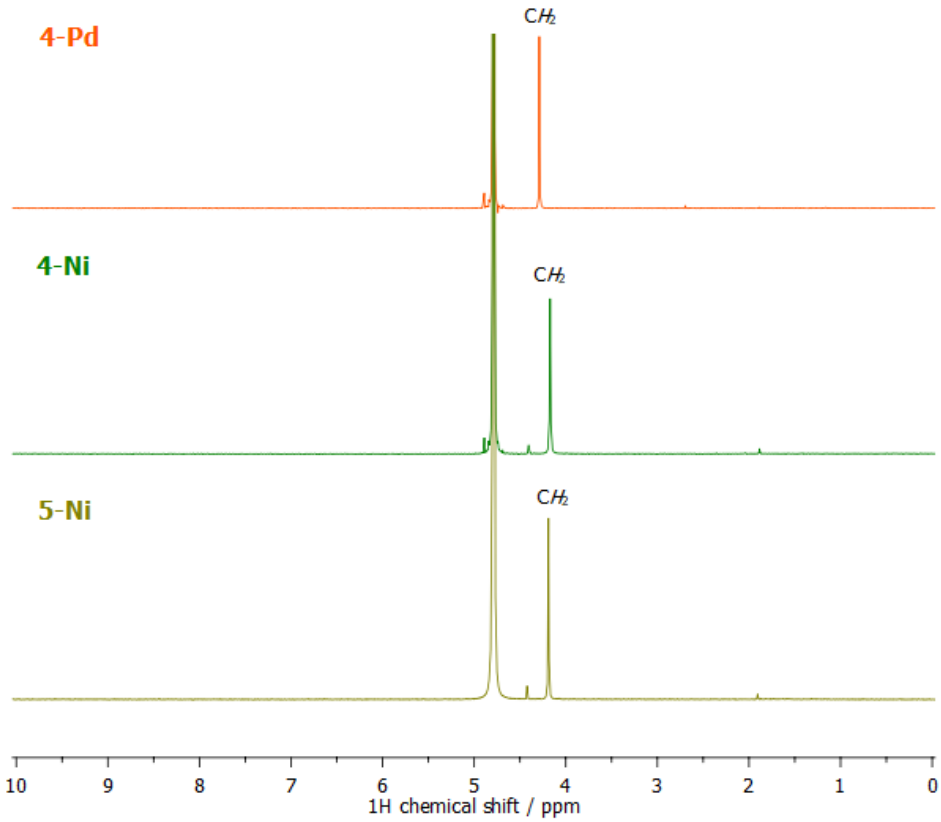


Figure S4. ^1H NMR spectra (400.1 MHz) of **4-Pd**, **4-Ni**, and **5-Ni**, measured in D_2O at ambient temperature.

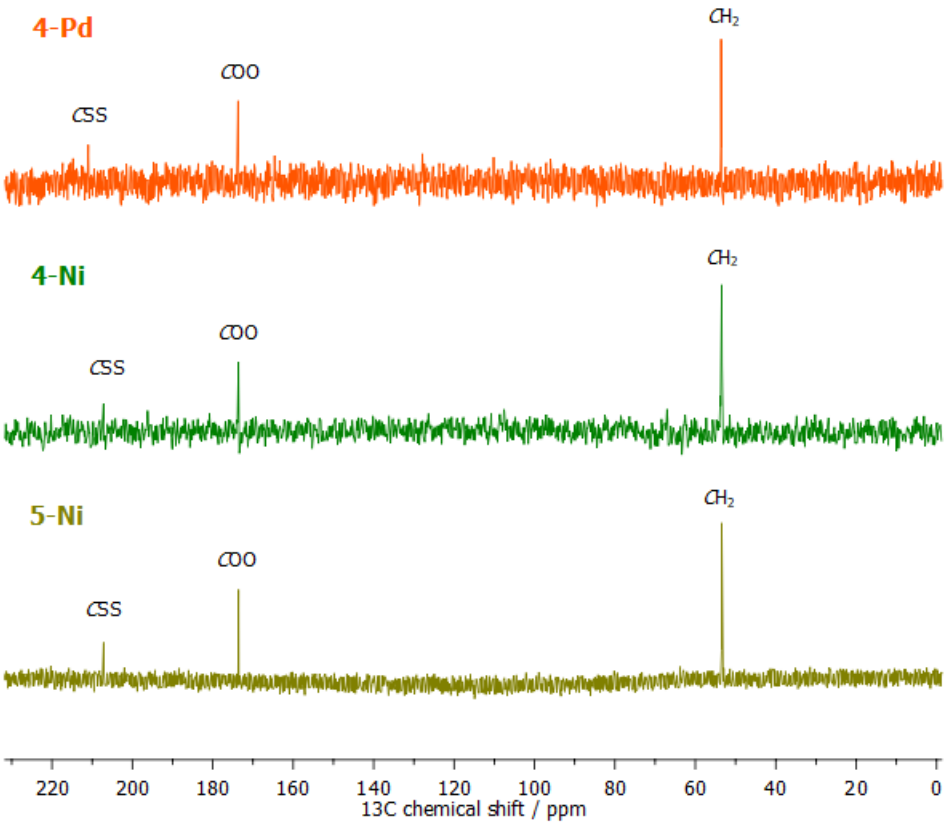


Figure S5. ^{13}C NMR spectra (100.6 MHz) of **4-Pd**, **4-Ni**, and **5-Ni**, measured in D_2O at ambient temperature.

Thermal analyses

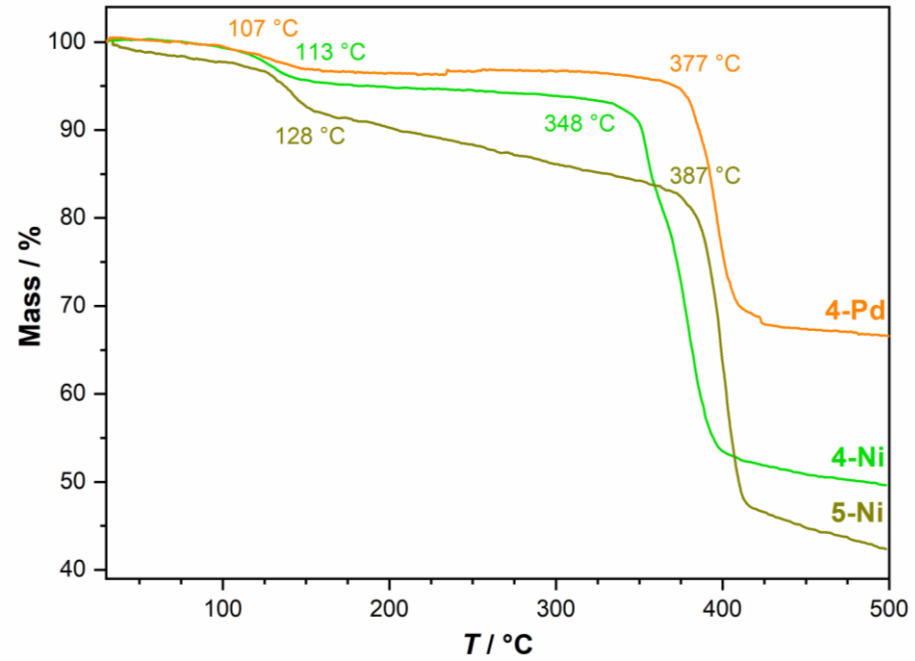


Figure S6. TG diagrams of **4-Pd** · $12H_2O$, **4-Ni** · $2H_2O$, and **5-Ni** · $2H_2O$, recorded under an inert atmosphere of nitrogen.

Single-crystal X-ray structural analyses

Table S1. Crystal data and details on structure refinement for the reported compounds.

Compound	**3-Pd · 6 H_2O**	**4-Pd · 14 H_2O**	**4-Ni · 14 H_2O**	**5-Ni · 2.5 acetone · 8.5 H_2O**
CCDC deposition number	2004119	2004120	2004121	2004122
Molecular formula sum	$C_{10}H_{22}N_2O_{14}PdS_4Zn$	$C_{10}H_{36}N_2O_{22}PdS_4Zn_2$	$C_{10}H_{36}N_2NiO_{22}S_4Zn_2$	$C_{17.5}H_{40}N_2NiO_{19}S_4Zn_2$
Formula weight / g mol^{-1}	694.30	901.79	854.10	900.20
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	C2/c
Cell metric *a* / Å	6.0814(5)	6.3065(2)	6.3059(2)	16.4930(6)
b / Å	6.7594(6)	13.5943(6)	13.5503(3)	27.4556(8)
c / Å	14.863(1)	16.9805(5)	16.9319(6)	17.4180(7)
α / deg.	95.993(7)	90	90	90
β / deg.	92.844(7)	97.902(3)	98.297(3)	117.645(3)
γ / deg.	115.909(6)	90	90	90
Cell volume / $Å^3$	543.46(8)	1441.96(9)	1431.63(8)	6986.9(5)
Molecules per cell *z*	1	2	2	8
Electrons per cell F_{000}	348	912	876	3704
Calcd. density ρ / g cm^{-3}	2.121	2.077	1.981	1.712
μ / mm^{-1} (Mo-K_α)	2.387	2.649	2.698	2.210
Crystal shape and color	yellow needle	yellow rod	green rod	light green plate
Crystal size / mm	0.20×0.06×0.04	0.30×0.06×0.03	0.44×0.07×0.06	0.24×0.12×0.03
θ range / deg.	2.772 … 29.231	2.997 … 27.000	2.859 … 28.499	1.986 … 24.999
Reflections collected	6482	8961	11956	16338
Reflections unique	2932	3139	3625	6139
Reflections with $I>2\sigma(I)$	2396	2560	3290	4676
Completeness of dataset	99.8%	99.8%	99.8%	99.6%
R_{int}	0.0598	0.0737	0.0399	0.0598
Parameters; Restraints	202; 39[a]	229; 14[a]	230; 14[a]	447; 25[b]
R_1 (all data, $I>2\sigma(I)$)	0.0642; 0.0467	0.0585; 0.0404	0.0322; 0.0274	0.0905; 0.0646
wR_2 (all data, $I>2\sigma(I)$)	0.1173; 0.1064	0.0969; 0.0869	0.0701; 0.0675	0.1826; 0.1568
GooF (F^2)	1.059	1.180	1.174	1.139
Max. residual peaks	–1.710; 1.050	–0.558; 0.505	–0.587; 0.438	–1.606; 1.712
Extinction coefficient	0.014(2)	–	0.0038(5)	–

[a] restraints on O-H distances within H_2O molecules; [b] restraints on C-C distances and anisotropic displacement parameters within a disordered acetone molecule.

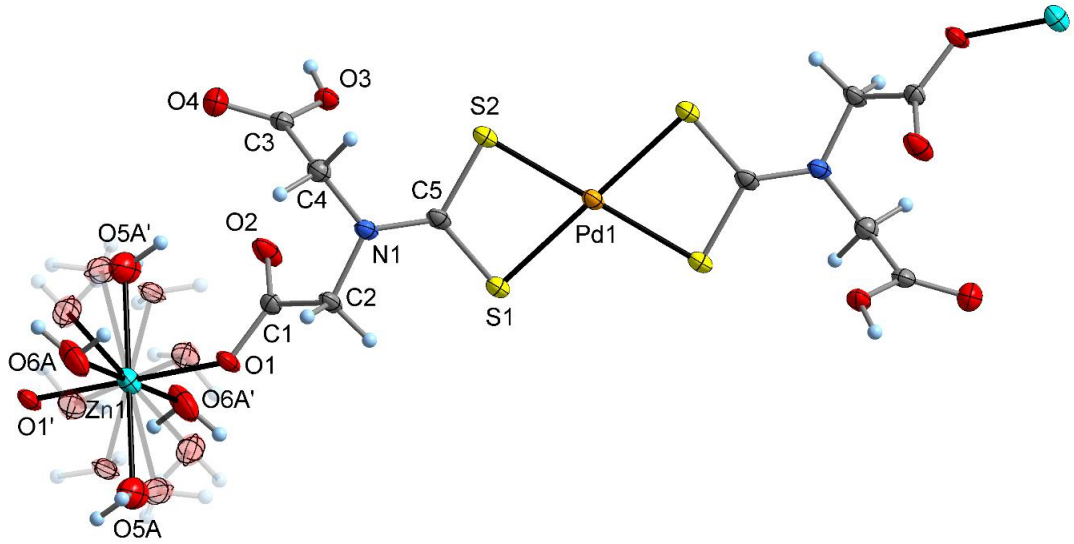


Figure S7. The asymmetric unit in the crystal structure of $Zn[Pd(HL)_2]$ (**3-Pd**) · $6H_2O$, showing the atom numbering scheme and rotational disorder of the $Zn(H_2O)_4$ fragment. Displacement ellipsoids drawn at the 50% probability level. Selected intermolecular distances (pm): Pd1-S1 231.6(1), Pd1-S2 232.4(1), Zn1-O1 212.3(3), Zn1-O5A 208(1), Zn1-O6B 206(1), C5-S1 172.5(4), C5-S2 171.2(4), C5-N1 132.7(5), S1-Pd1-S2 75.51(4), S1-Pd1-S2'' 104.49(4), O1-Zn1-O5A 89.3(3), O1-Zn1-O5A' 90.7(3), O1-Zn1-O6A 84.9(3), O1-Zn1-O6A' 95.1(3), O5A-Zn1-O6A 88.6(5), O5A-Zn1-O6A' 91.4(5), S1-C5-S2 111.5(2). Symmetry codes: ' 1–*x*, –*y*, –*z*; '' –*x*, 1–*y*, 1–*z*.

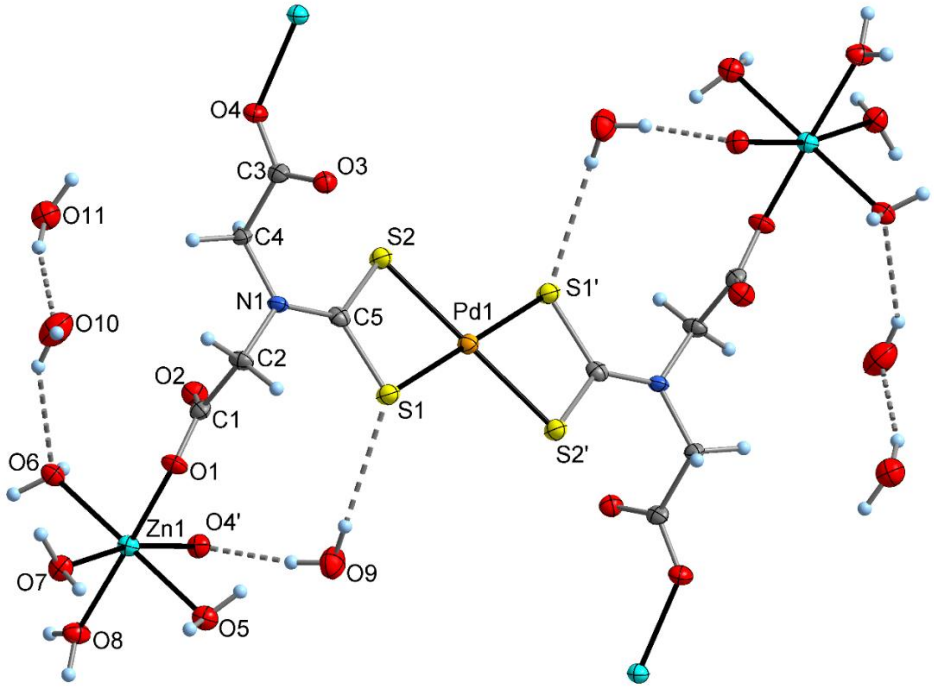


Figure S8. Molecular structure of $Zn_2[Pd(L)_2]$ (**4-Pd**) · $14H_2O$ in the crystal, showing the atom numbering scheme. Displacement ellipsoids drawn at the 50% probability level. Selected intermolecular distances (pm) and angles (deg.): Pd1-S1 232.5(1), Pd1-S2 2231.1(1), Zn1-O1 204.2(3), Zn1-O4'' 207.1(3), Zn1-O5 218.3(3), Zn1-O6 211.7(3), Zn1-O7 212.3(3), Zn1-O8 209.5(3), C5-S1 173.2(5), C5-S2 171.9(5), C5-N1 131.2(6), S1-Pd1-S2 75.80(4), S1-Pd1-S2' 104.20(4), O1-Zn1-O4'' 97.5(1), O1-Zn1-O5 88.1(1), O1-Zn1-O6 91.0(1), O1-Zn1-O7 90.2(1), O1-Zn1-O8 173.0(1), O4''-Zn1-O5 84.7(1), O4''-Zn1-O6 97.1(1), O4''-Zn1-O7 168.2(1), O4''-Zn1-O8 88.9(1), O5-Zn1-O6 178.0(1), O5-Zn1-O7 86.6(1), O5-Zn1-O8 89.6(1), O6-Zn1-O7 91.6(1), O6-Zn1-O8 91.1(1), O7-Zn1-O8 83.1(1), S1-C5-S2 111.2(3). Symmetry codes: ' 2–*x*, 1–*y*, 1–*z*; '' 1.5–*x*, –0.5+*y*, 0.5–*z*.

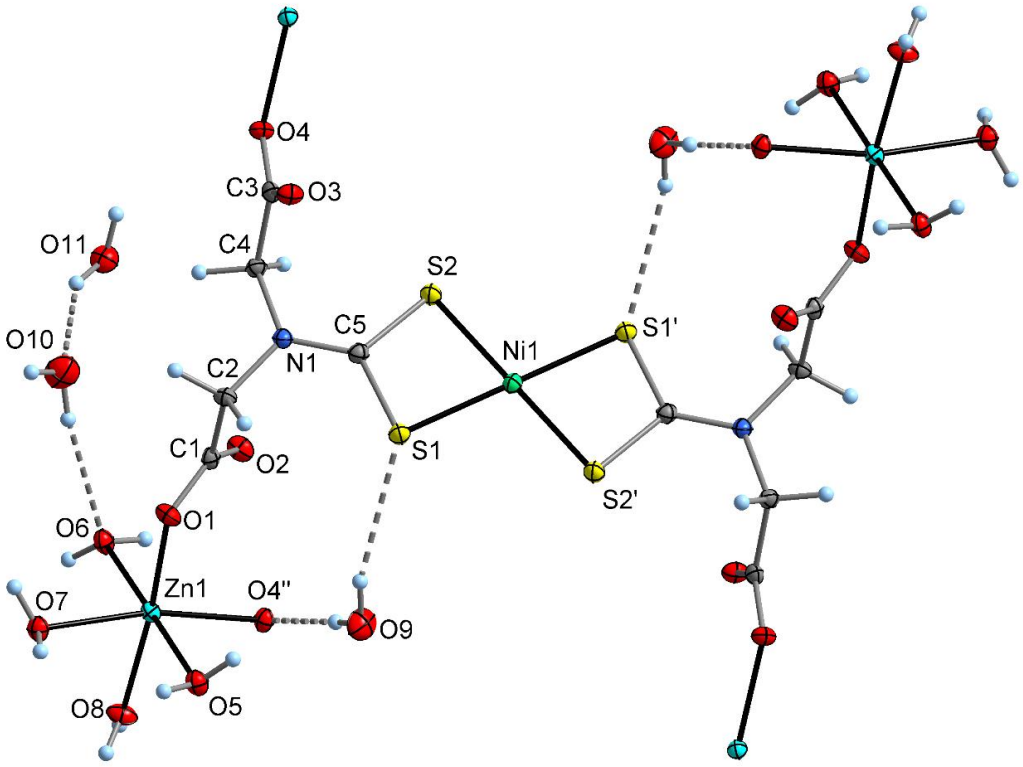


Figure S9. Molecular structure of $Zn_2[Ni(L)_2]$ (**4-Ni**) · $14H_2O$ in the crystal, showing the atom numbering scheme. Displacement ellipsoids drawn at the 50% probability level. Selected intermolecular distances (pm) and angles (deg.): Ni1-S1 220.79(5), Ni1-S2 219.12(5), Zn1-O1 204.0(2), Zn1-O4'' 207.1(2), Zn1-O5 218.3(2), Zn1-O6 212.1(2), Zn1-O7 212.3(2), Zn1-O8 209.2(2), C5-S1 172.3(2), C5-S2 171.6(2), C5-N1 131.3(3), S1-Ni1-S2 79.60(2), S1-Ni1-S2' 100.40(2), O1-Zn1-O4'' 97.34(6), O1-Zn1-O5 88.22(6), O1-Zn1-O6 90.91(6), O1-Zn1-O7 90.54(6), O1-Zn1-O8 173.27(6), O4''-Zn1-O5 84.60(6), O4''-Zn1-O6 96.73(6), O4''-Zn1-O7 168.12(6), O4''-Zn1-O8 88.85(6), O5-Zn1-O6 178.49(6), O5-Zn1-O7 86.79(6), O5-Zn1-O8 89.73(6), O6-Zn1-O7 91.99(6), O6-Zn1-O8 91.00(6), O7-Zn1-O8 82.94(6), S1-C5-S2 110.0(1). Symmetry codes: ' 2–*x*, 1–*y*, 1–*z*; '' 1.5–*x*, –0.5+*y*, 0.5–*z*.

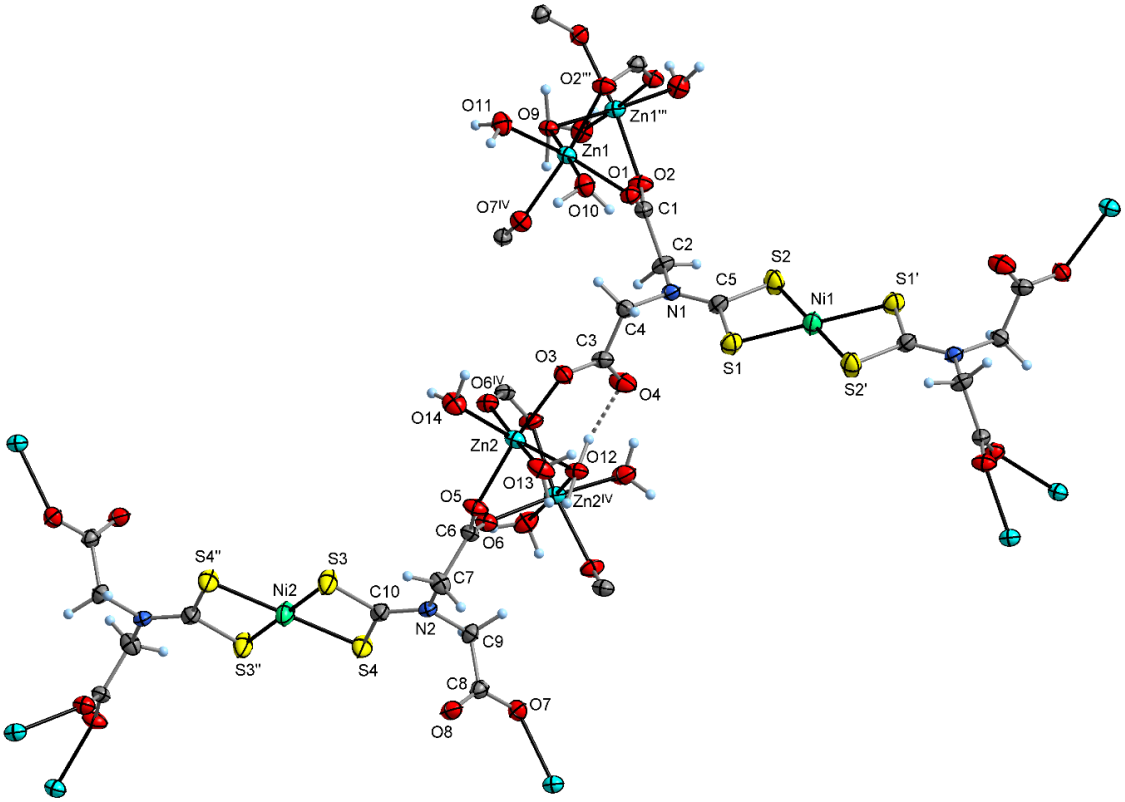


Figure S10. Molecular structure of $Zn_2[Ni(L)_2]$ (**5-Ni**) · 2.5 acetone · 8.5 H_2O in the crystal, showing the atom numbering scheme. Displacement ellipsoids drawn at the 50% probability level, non-coordinated solvent of crystallization omitted for clarity. Selected intermolecular distances (pm) and angles (deg.): Ni1-S1 220.3(2), Ni1-S2 219.7(2), Ni2-S3 220.2(2), Ni2-S4 219.3(2), Zn1-O1 206.2(5), Zn1-O2''' 206.3(5), Zn1-O7^{IV} 214.8(5), Zn1-O9 212.6(4), Zn1-O10 203.9(5), Zn1-O11 205.5(5), Zn2-O3 214.3(5), Zn2-O5 205.3(5), Zn2-O6^{IV} 207.1(5), Zn2-O12 216.7(4), Zn2-O13 206.9(5), Zn2-O14 205.1(5), C5-S1 171.3(7), C5-S2 170.4(7), C10-S3 171.2(7), C10-S4 170.3(7), C5-N1 133.5(9), C10-N2 132.9(9), S1-Ni1-S2 79.51(7), S1-Ni1-S2' 100.49(7), S3-Ni2-S4 79.65(7), S3-Ni2-S4'' 100.35(7), O1-Zn1-O2''' 96.8(2), O1-Zn1-O7^{IV} 88.2(2), O1-Zn1-O9 92.2(2), O1-Zn1-O10 85.4(2), O1-Zn1-O11 171.9(2), O2'''-Zn1-O7^{IV} 173.1(2), O2'''-Zn1-O9 89.0(2), O2'''-Zn1-O10 93.8(2), O2'''-Zn1-O11 88.3(2), O7^{IV}-Zn1-O9 86.1(2), O7^{IV}-Zn1-O10 91.3(2), O7^{IV}-Zn1-O11 87.2(2), O9-Zn1-O10 176.5(2), O9-Zn1-O11 94.1(2), O10-Zn1-O11 88.1(2), O3-Zn2-O5 171.1(2), O3-Zn2-O6^{IV} 91.5(2), O3-Zn2-O12 89.8(2), O3-Zn2-O13 84.8(2), O3-Zn2-O14 89.8(2), O5-Zn2-O6^{IV} 97.1(2), O5-Zn2-O12 88.6(2), O5-Zn2-O13 86.7(2), O5-Zn2-O14 93.0(2), O6^{IV}-Zn2-O12 88.0(2), O6^{IV}-Zn2-O13 174.2(2), O6^{IV}-Zn2-O14 84.3(2), O12-Zn2-O13 96.5(2), O12-Zn1-O14 172.3(2), O13-Zn2-O14 91.1(2), S1-C5-S2 110.9(4), S3-C10-S4 111.0(4). Symmetry codes: ' 1.5–*x*, 1.5–*y*, 1–*z*; '' 0.5–*x*, 0.5–*y*, –*z*; '''2–*x*, *y*, 1.5–*z*; ^{IV} 1–*x*, *y*, 0.5–*z*.