Supporting Information for:

Capture of Ni^{II}, Cu^{I} and Zn^{II} by Thiolate Sulfurs of an $\text{N}_2\text{S}_2\text{Ni}$ Complex: A Role for a Metallothiolate Ligand in the Acetyl-coenzyme A Synthase Active Site

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Experimental Section.

Figure S1. Vis-UV of 0.3 mM methanol solutions of (**A**) [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl], (**B**) **Ni-1**, (**C**) [(**Ni-1**)$_2$Ni][2Br], (**D**) [(**Ni-1**)$_3$(CuBr)$_2$]. (**Ni-1** = (bmedaco)Ni).

Figure S2. Vis-UV of **(A)** 0.3 mM methanol solution of [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl], **(B)** [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl] + NiCl$_2$, **(C)** [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl] + CuBr.

Figure S3. Vis-UV of (**A**) 0.3 mM methanol solution of [(**Ni-1**)$_2$Ni][2Br], (B) [(**Ni-1**)$_2$Ni][2Br] + ZnCl$_2$, (**C**) [(**Ni-1**)$_2$Ni][2Br] + CuBr. The diminished peaks of (**B**) with respect to (**A**) are a result of dilution.

Figure S4. Vis-UV of **(A)** 0.3 mM methanol solution of [(**Ni-1**)$_3$(CuBr)$_2$], **(B)** [(**Ni-1**)$_3$(CuBr)$_2$] + ZnCl$_2$, **(C)** [(**Ni-1**)$_3$(CuBr)$_2$] + NiCl$_2$. The diminished peaks of **(B)** and **(C)** with respect to (**A**) are a result of dilution.

Figure S5. Vis-UV spectra of **(A) Ni-1** + 0.39 eq. CuBr + 0.28 eq. of NiCl$_2$, **(B) Ni-1** + 0.39 eq. CuBr + 0.57 eq. of NiCl$_2$ and **(C) Ni-1** + 0.77 eq. CuBr + 0.28 eq. of NiCl$_2$. Insufficient Cu^{I} in **(A)** and **(B)** results in a mixture of [(**Ni-1**)$_3$(CuBr)$_2$] and [(**Ni-1**)$_2$Ni][2Br].

Figure S6. Vis-UV spectra of **Ni-1** + 0.67 eq. CuBr + excess NiCl$_2$. The small peak at 300 nm is a charge transfer band indicating the formation of some [(**Ni-1**)$_2$Ni][2Br] but disappears with added CuBr.

Figure S7. Vis-UV spectra of [(**Ni-1**)$_2$Ni]$^{2+}$(Br-)$_2$ in MeOH before and after addition of 6 equivalents of 1,10-phenanthroline.

Figure S8. ORTEP plot of [(bmedaco)Ni]$_3$(CuBr)$_2$ at 50%.

Figure S9. Ball and stick drawing of [(bmedaco)Ni]$_3$(CuBr)$_2$ with atoms labeled.

Figure S10. Unit cell of [(bmedaco)Ni]$_3$(CuBr)$_2$.

Table S1. CIF file.

Experimental Section

General Methods and Materials. While the compounds are not exceedingly air sensitive, all syntheses and manipulations of materials were carried out under an Argon atmosphere using Schlenk techniques or a glovebox. Solvents were dried under a dinitrogen atmosphere prior to use according to published procedures.[c] $ZnCl_2$, CuBr (Aldrich Chemical Co.) and $NiCl_2 \cdot 6H_2O$ (J. T. Baker) were used as received. The dithiol (H_2bmedaco) and its nickel complex, (**Ni-1**), were synthesized according to published procedures.[d]

Physical Measurements. Vis/UV spectra were recorded on a Hewlett-Packard HP8452A diode array spectrophotometer. Elemental Analysis was performed by Canadian Microanalytical Systems in Delta, British Columbia, Canada. Mass Spectral analyses were done at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Electrospray Ionization mass spectra were recorded using a MDS-Series QStar Pulsar with a spray voltage of 5 KeV.

Syntheses. [(**Ni-1**)$_2$Ni][2Br][a] and [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl][b] were synthesized according to previously reported methods.

Preparation of [(Ni-1)$_3$(CuBr)$_2$]. Under an inert atmosphere **Ni-1** (0.1000 g, 0.3436 mmol) was added to a Schlenk flask and dissolved in 15 mL of CH_3CN. To this deep purple solution a pale green CH_3CN solution of CuBr (0.025 g, 0.1743 mmol) was added dropwise resulting in a dark green solution with brown precipitate. The solution was stirred vigorously for several hours. The solvent was then evaporated, and the brown solid was washed with hexane. Yield: 0.0828 g, 58.8 %. Crystals of X-ray quality were obtained from slow evaporation of ether into a CH_2Cl_2 solution of the product. Vis-UV (methanol), nm ($M^{-1}cm^{-1}$): 330 (2650), 396 (1680), 580 (815). Elemental Anal. Calculated (found) for $Ni_3Cu_2C_{30}H_{120}N_6S_6Br_2$: C, 31.06 (30.71); N, 7.24 (6.37); H, 5.21 (5.22). Mass spectrum (*m/z*): 500 {(**Ni-1**)$_3$Cu$_2$}$^{2+}$; 1079 {(**Ni-1**)$_3$Cu$_2$Br}$^{+}$.

Displacement Reactions. 0.3 mM stock solutions were made by dissolving 0.002 g, 0.0035 g, and 0.0032 g of [(**Ni-1**)$_2$Ni][2Br], [(**Ni-1**)$_3$(CuBr)$_2$], and [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl] respectively in a 10 mL of MeOH using a volumetric flasks. 0.6 mM solutions were made by dissolving 0.0036 g of $NiCl_2{\cdot}6H_2O$ in 25 mL of MeOH, 0.009 g CuBr in 100 mL of CH_3CN, and 0.008 g $ZnCl_2$ in 100 mL MeOH. 2mL of metal complex was added to 2 mL of metal solution. The reactions were carried out at 22 ºC. Any observed color changes were on time of mixing and followed by spectral changes in the visible region. See Figures S2-S4.

Metal Competition. Using a 11 mM CuBr solution in CH_3CN, 5.7 mM $NiCl_2{\cdot}6H_2O$ in MeOH and 1.3 mM Ni-1 in methanol, various ratios of Ni^{II} and Cu^{I} were reacted with **Ni-1**. [**(Ni-1)**$_3$(CuBr)$_2$] requires 0.67 equivalents of Cu^{I} to react with one equivalent of **Ni-1**, and [(**Ni-1**)$_2$Ni]$^{++}$ requires 0.5 equivalents of Ni^{II} to react with **Ni-1**. The first sample contained 90 μL Cu^{I} (0.39 eq.), 130 μL Ni^{II} (0.28 eq.) and 130 μL MeOH. To this was added 2 mL of **Ni-1**. Insufficient Cu^{I} and Ni^{II} resulted in a mixture of [**(Ni-1)**$_3$(CuBr)$_2$] and [(**Ni-1**)$_2$Ni]$^{++}$. The second sample contained 90 μL Cu^{I} (0.39 eq.) and 260 μL Ni^{II} (0.57 eq.) to which 2 mL of **Ni-1** was added. Insufficient Cu^{I} and excess Ni^{II} also resulted in a mixture which was visible to the eye due to the brownish pink color. The third sample contained 180 μL Cu^{I} (0.77 eq.), 130 μL Ni^{II} (0.28 eq.) and 40 μL MeOH. To this was also added 2 mL of **Ni-1**. Excess Cu^{I} and insufficient Ni^{II} produces [**(Ni-1)**$_3$(CuBr)$_2$]. Reactions were followed by spectral changes in the vis-UV (See Figure S5), and total volumes were kept constant by the addition of MeOH. Metal competition was also tested with sufficient Cu^{I} and excess Ni^{II}. A 0.6 mM solution was made by dissolving 0.0018 g of (**Ni-1**) in 10 mL of MeOH. Next a slurry was made by adding 0.0436 g $NiCl_2{\cdot}6H_2O$ to 10 mL of a 0.6mM CuBr solution in CH_3CN. 1.33 mL of the Ni^{II}, Cu^{I} solution was added to 2 ml of 0.6mM Ni-1 resulting in almost a 40 fold excess of Ni^{II} and 0.66 eq. of Cu^{I}. Even with an excess of Ni^{II}, [**(Ni-1)**$_3$(CuBr)$_2$] is formed (See Figure S6). This is submitted as further evidence of the preference of the N_2S_2Ni for Cu^{I} over Ni^{II}.

Metal Extraction. 0.0063 g (**Ni-1**) was dissolved in 3mL of distilled MeOH. To this solution was added 3 equivalents (0.0126 g) of 1,10-phenanthroline which did not result in any vis-UV spectral changes. 0.0089 g of [(**Ni-1**)$_2$Ni][2Br] was dissolved in 24 mL of distilled MeOH. To this solution was added 3 equivalents (0.0062 g) 1,10-phenanthroline which produced a bleaching of the yellow brown color. The reaction was not instantaneous and did not appear complete, so another 3 equivalents were added and allowed to stir for longer period of time. The resulting solution was salmon pink indicating the formation of $Ni(phen)_3^{2+}$. Addition of $NiCl_2$ reconstituted the [(**Ni-1**)$_2$Ni][2Br] spectral peaks. Reactions were followed by vis-UV spectroscopy (see Figure S7). The addition of 6 equivalents (0.0054 g) of 1,10-phenanthroline to 0.0058 g [(**Ni-1**)$_3$(CuBr)$_2$] in 25 mL of MeOH did not remove Cu^{I}.

References:

a) Farmer, P. J.; Solouki, T.; Mills, D. K.; Soma, T.; Russell, D. H.; Reibenspies J. H.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4601.

b) Tuntulani, T.; Reibenspies, J. H.; Farmer, P. J.; Darensbourg, M. Y. *Inorg. Chem.* **1992**, *31*, 3497.

c) Gordan, A. J.; Ford, R. A. *The Chemist's Companion* (Wiley and Sons, New York, 1972) pp. 430-437.

d) Mills, D. K.; Font, I.; Farmer, P. J.; Tuntulani, T.; Buonomo, R. M.; Goodman, D. C.; Musie, Grapperhaus, C. A.; Maguire, M. J.; Lai, C.; Hatley, M. L.; Smee, J. J.; Bellefuille, J. A.; Darensbourg, M. Y. *Inorg. Synth.* **1998**, *32*, 89-98.

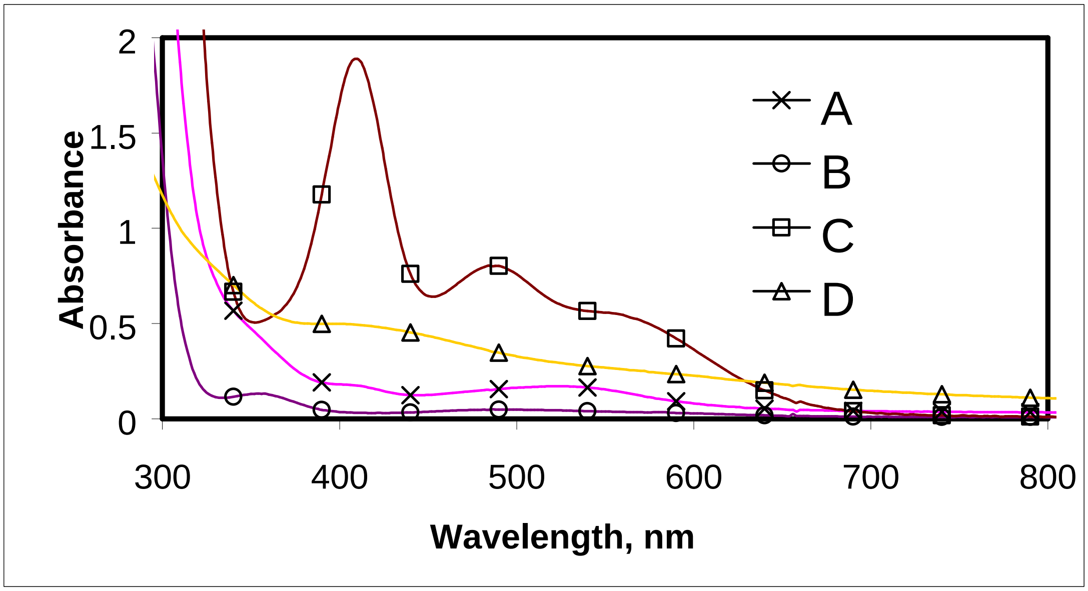

Figure S1. Vis-UV of 0.3 mM methanol solutions of **(A)** [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl], **(B)** **Ni-1**, **(C)** [(**Ni-1**)$_2$Ni][2Br], **(D)** [(**Ni-1**)$_3$(CuBr)$_2$].

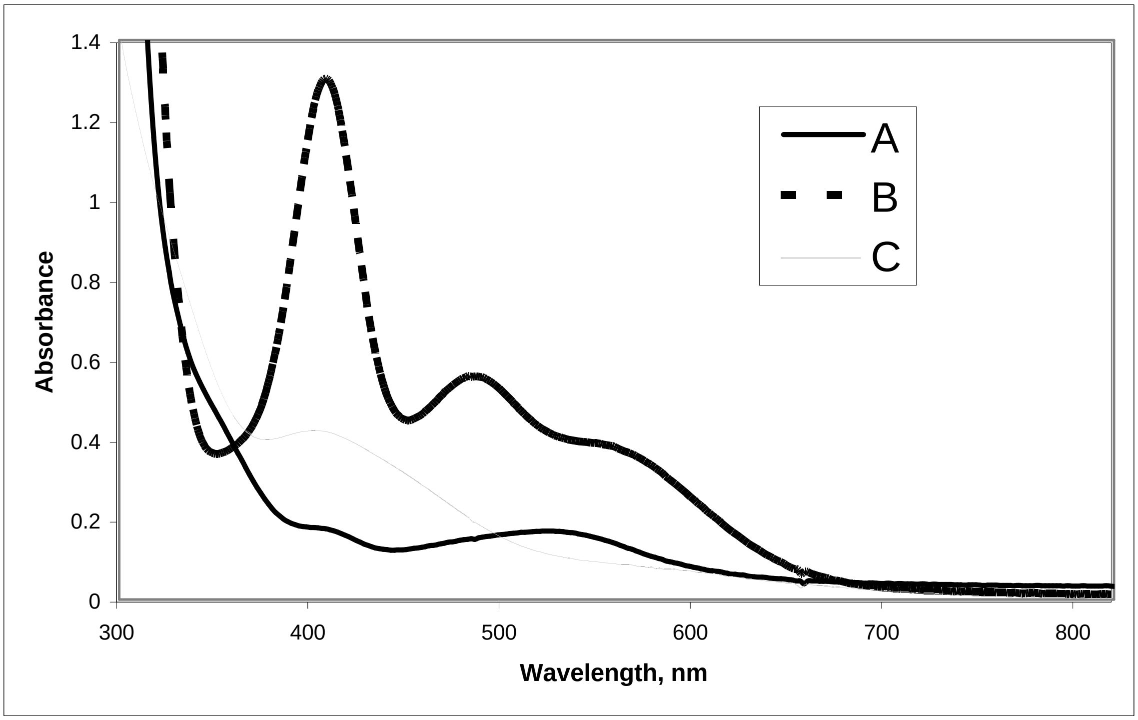

Figure S2. Vis-UV of **(A)** 0.3 mM methanol solution of [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl], **(B)** [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl] + NiCl$_2$, **(C)** [(**Ni-1**)$_3$(ZnCl)$_2$][2Cl] + CuBr.

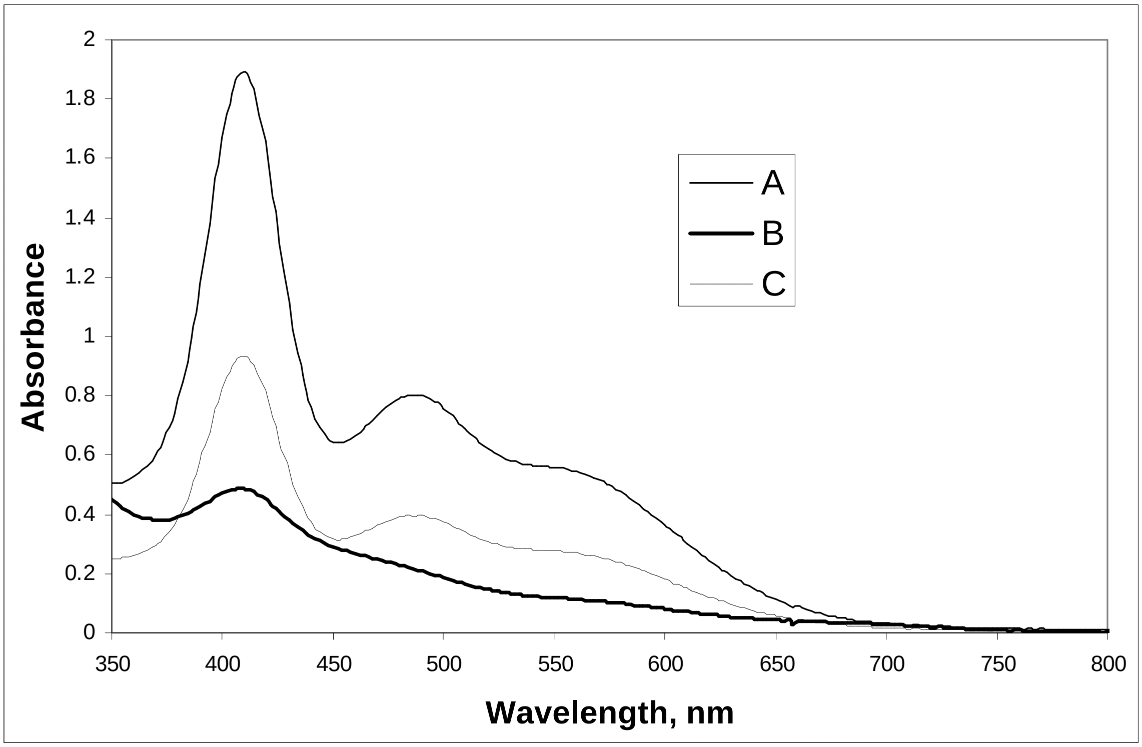

Figure S3. Vis-UV of (**A**) 0.3 mM methanol solution of [(**Ni-1**)$_2$Ni][2Br], (**B**) [(**Ni-1**)$_2$Ni][2Br] + ZnCl$_2$, (**C**) [(**Ni-1**)$_2$Ni][2Br] + CuBr. The diminished peaks of (**B**) with respect to (**A**) are a result of dilution.

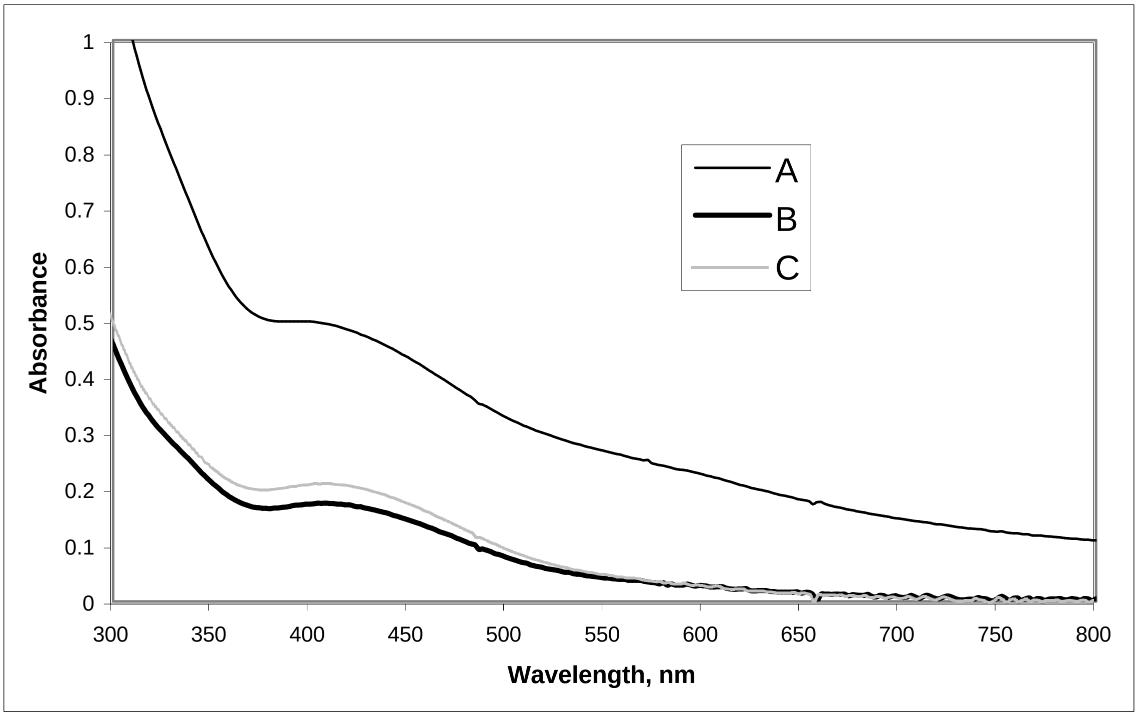

Figure S4. Vis-UV of **(A)** 0.3 mM methanol solution of [(**Ni-1**)$_3$(CuBr)$_2$], **(B)** [(**Ni-1**)$_3$(CuBr)$_2$] + ZnCl$_2$, **(C)** [(**Ni-1**)$_3$(CuBr)$_2$] + NiCl$_2$. The diminished peaks of **(B)** and **(C)** with respect to (**A**) are a result of dilution.

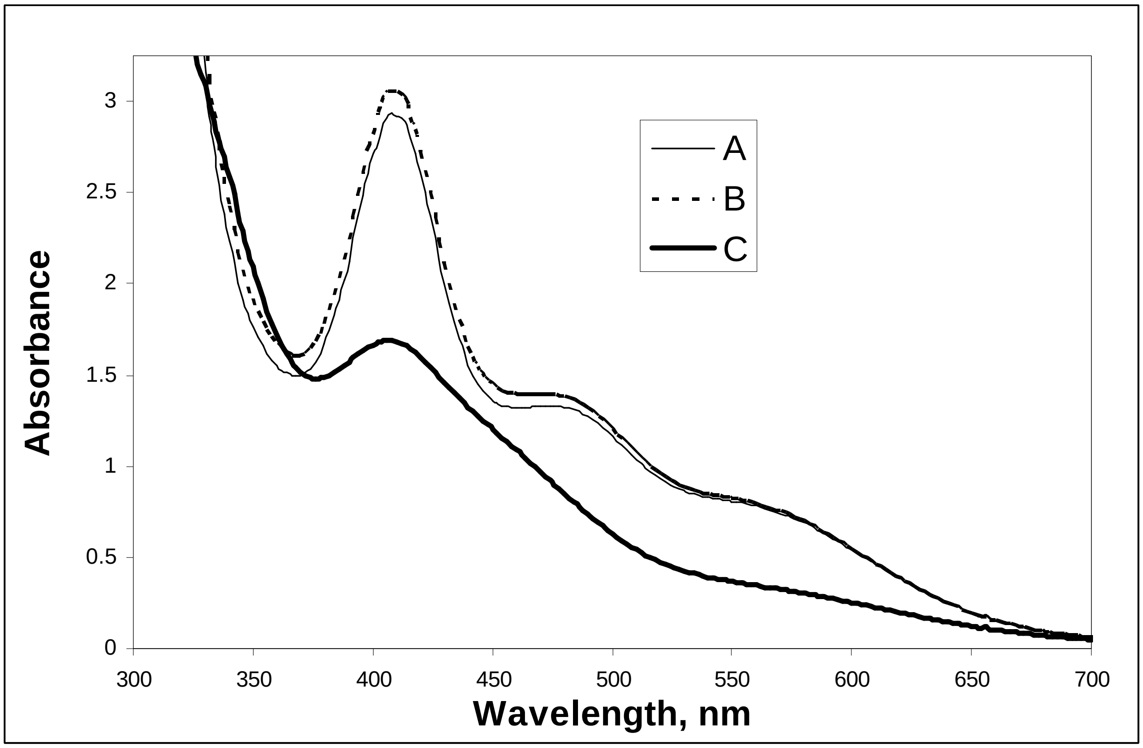

Figure S5. Vis-UV spectra of **(A) Ni-1** + 0.39 eq. CuBr + 0.28 eq. of $NiCl_2$, **(B) Ni-1** + 0.39 eq. CuBr + 0.57 eq. of $NiCl_2$ and **(C) Ni-1** + 0.77 eq. CuBr + 0.28 eq. of $NiCl_2$. Insufficient Cu^I in **(A)** and **(B)** results in a mixture of [(**Ni-1**)$_3$(CuBr)$_2$] and [(**Ni-1**)$_2$Ni][2Br].

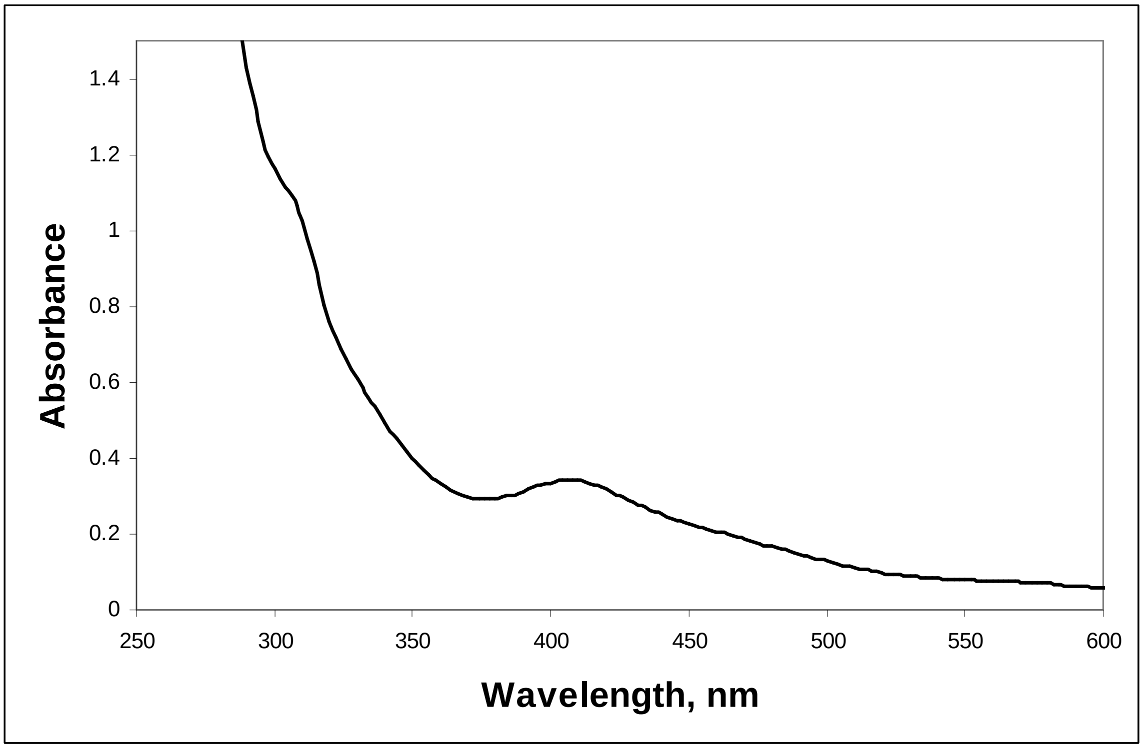

Figure S6. Vis-UV spectra of **Ni-1** + 0.67 eq. CuBr + excess $NiCl_2$. The slight peak at 300 nm is a charge transfer band indicating the formation of some [(**Ni-1**)$_2$Ni][2Br] but disappears with added CuBr.

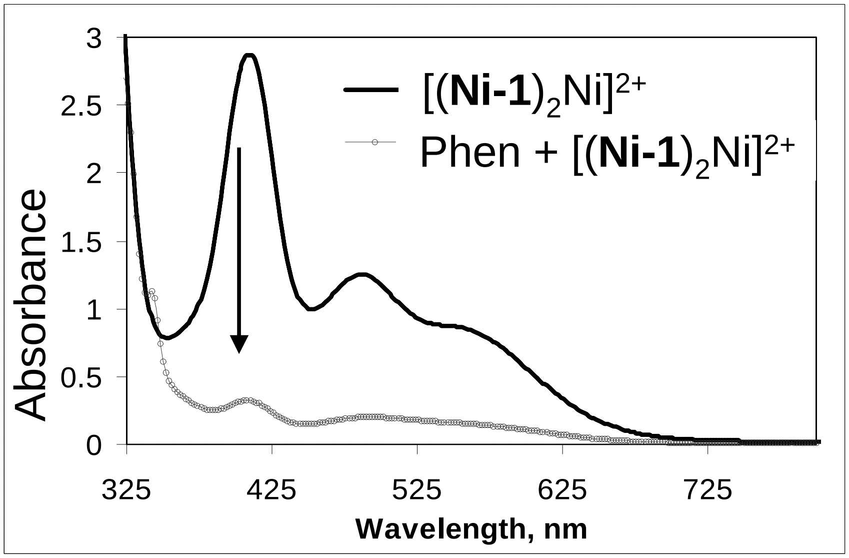

Figure S7. Vis-UV spectra of [(**Ni-1**)$_2$Ni]$^{2+}$(Br-)$_2$ in MeOH before and after addition of 6 equivalents of 1,10-phenanthroline.

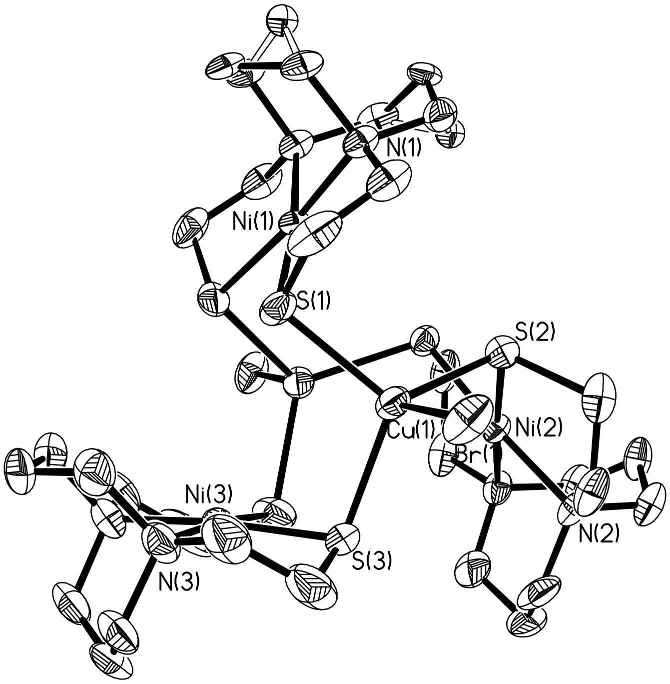

Figure S8. ORTEP plot of $[(bmedaco)Ni]_3(CuBr)_2$.

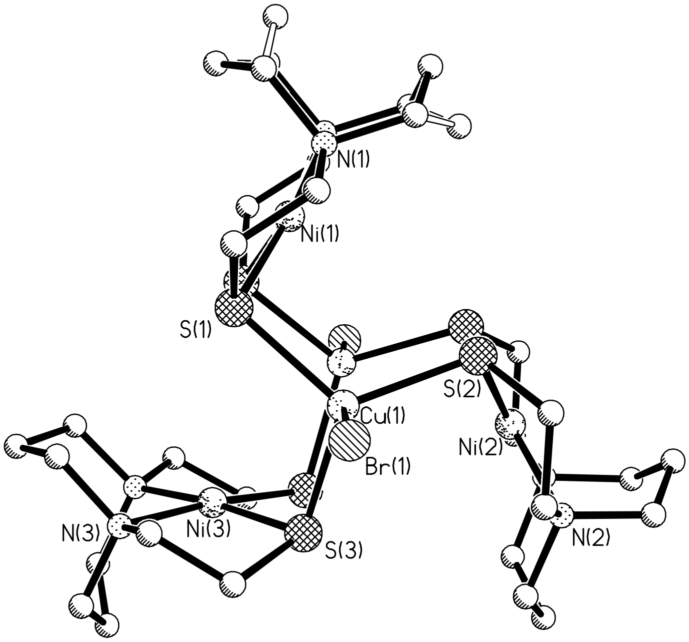

Figure S9. Ball and stick drawing of [(bmedaco)Ni]$_3$(CuBr)$_2$ with atoms labeled.

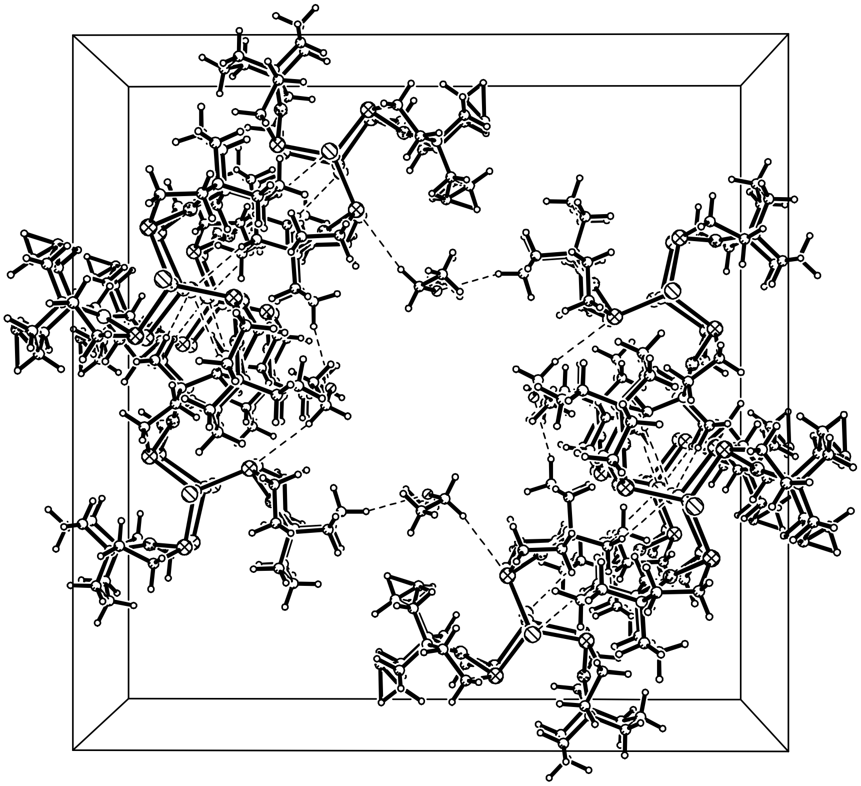

Figure S10. Unit cell of [(bmedaco)Ni]$_3$(CuBr)$_2$.

Table S1. Crystal data and structure refinement for [(bmedaco)Ni]$_3$(CuBr)$_2$•2 Et$_2$O

Identification code	mr02	
Empirical formula	$C_{38} H_{80} Br_2 Cu_2 N_6 Ni_3 O_2 S_6$	
Formula weight	1308.47	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 4/m	
Unit cell dimensions	a = 26.1834(13) Å	α= 90°.
	b = 26.1834(13) Å	β= 90°.
	c = 15.5725(9) Å	g = 90°.
Volume	10676.0(10) Å^3	
Z	8	
Density (calculated)	1.628 Mg/m^3	
Absorption coefficient	3.592 mm^{-1}	
F(000)	5392	
Theta range for data collection	1.52 to 24.99°.	
Index ranges	-31<=h<=24, -31<=k<=30, -15<=l<=18	
Reflections collected	27161	
Independent reflections	4799 [R(int) = 0.1329]	
Completeness to theta = 24.99°	98.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4799 / 10 / 276	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0519, wR2 = 0.1447	
R indices (all data)	R1 = 0.0701, wR2 = 0.1601	
Largest diff. peak and hole	2.018 and -0.952 e.Å^{-3}	