

## Supplementary Materials for

### Zinc/Nickel Exchange and Ligand Cannibalism in $N_2S_2O_{1,2}$ Donor Ligand Sets

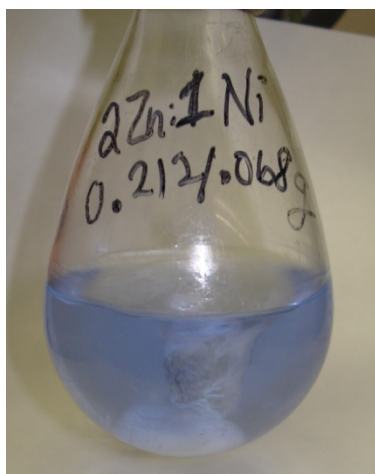
Elky Almaraz, Jason A. Denny, William S. Foley, Joseph H. Reibenspies, Nattamai Bhuvanesh, Marcetta Y. Darensbourg\*

*Department of Chemistry, Texas A&M University, College Station, Texas 77843*

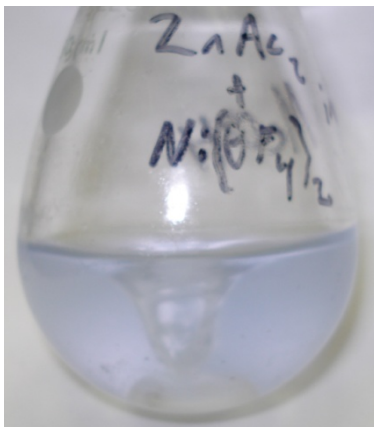
\* To whom correspondence should be addressed. E-mail: [marcetta@mail.chem.tamu.edu](mailto:marcetta@mail.chem.tamu.edu)



**Figure S1.** Schlenk flasks containing the reaction mixtures from synthetic route (b) on the left and route (b') on the right were photographed against a colored background to highlight the clear and cloudy makeup of each colorless solution.



**Figure S2.** Reaction flask containing the 2 Zn: 1 Ni zinc displacement reaction solution in CH<sub>3</sub>OH. The blue color was observed upon immediate addition of the light green Ni to the colorless Zn solution.



**Figure S3.** A Schlenk flask containing the zinc displacement reaction of Ni(BF<sub>4</sub>)<sub>2</sub> (light green) with Zn-1'-Ac<sub>2</sub> (colorless) in CH<sub>3</sub>OH. The blue color was observed after approx. 30 min of reaction time.

**Table S1.** Selected Bond Lengths (Å) for [Zn-1']<sub>2</sub>, Zn-1'-Ac, and Zn-1'-Ac<sub>2</sub>.

	[Zn-1'] <sub>2</sub>	Zn-1'-Ac	Zn-1'-Ac <sub>2</sub>
Zn(1) – S(thiolate)	2.307* 2.496**	2.263	--
Zn(1) – S(thioether)	--	2.587	2.552 2.601
Zn(1) – O(1)	--	1.983	2.039 2.044

\* terminal thiolate, \*\* bridging thiolate

**Table S2.** Summary of Crystallographic Data.

	Zn-1'-Ac <sub>2</sub>	Ni-1'-Ac <sub>2</sub>
empirical formula	C <sub>15</sub> H <sub>30</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub> Zn	C <sub>13</sub> H <sub>28</sub> N <sub>2</sub> O <sub>7</sub> S <sub>2</sub> Ni
formula weight	463.90	447.20
temperature (K)	110(2)	110(2)
wavelength (Å)	1.54178	0.71073
<i>Z</i>	2	4
<i>D</i> <sub>calcd</sub> (g / cm <sup>3</sup> )	1.559	1.610
$\mu$ (mm <sup>-1</sup> )	4.001	1.315
crystal system	Triclinic	Monoclinic
space group	P-1	P2(1)
<i>a</i> (Å)	7.5042(14)	7.731(2)
<i>b</i> (Å)	8.0905(15)	7.703(2)
<i>c</i> (Å)	16.774(4)	30.984(9)
$\alpha$ (°)	78.684(11)	90
$\beta$ (°)	81.945(11)	90.282(5)
$\gamma$ (°)	86.515(10)	90
<i>V</i> (Å <sup>-3</sup> )	988.2(3)	1845.1(9)
Goodness-of-fit	1.067	1.003
R1 <sup>a</sup> , wR2 <sup>b</sup> (%) [ <i>I</i> > 2σ( <i>I</i> )]	0.0368, 0.0982	0.0572, 0.1238
R1 <sup>a</sup> , wR2 <sup>b</sup> (%) (all data)	0.0415, 0.1005	0.0629, 0.1290

<sup>a</sup> R1 =  $\sum||F_o| - |F_c||/\sum F_o$ . <sup>b</sup> wR2 =  $[\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$ .