

## Nickel mediated sulfur–selenium and sulfur–sulfur bond formation

Chia-Huei Lai, Joseph H. Reibenspies and Marcetta Y. Darensbourg\*

Department of Chemistry, Texas A&amp;M University, College Station, Texas 77843, USA.

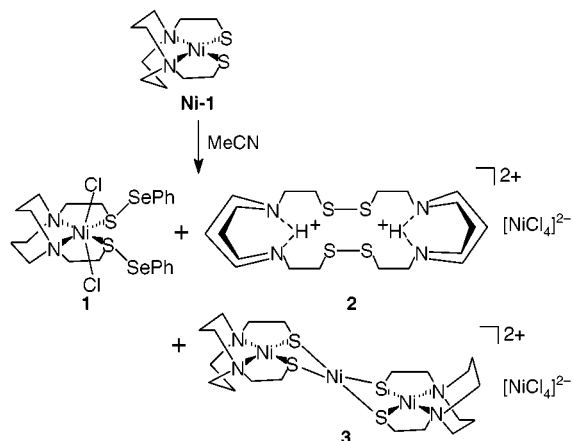
E-mail: marcetta@mail.chem.tamu.edu

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**Electrophilic addition of the PhSeCl to a nickel dithiolate yields *S,S'*-bis(phenylselenenyl)-*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane nickel(II) dichloride and a dimeric, intermolecular bis-disulfide which results from ligand oxidation.**

To extend the well known S-based nucleophilicity of [*N,N'*-bis(mercaptoethyl)-1,5-diazacyclooctane]nickel(II), (bme-daco)Ni or **Ni-1**,<sup>1</sup> especially with regard to developing reactive ligand functionalities, we explored the reactivity of **Ni-1** with PhSeCl, Scheme 1. The desired nickel-bound selenosulfide **1**, a moiety which should be capable of subsequent oxidative addition to low-valent metals and thus of potential usefulness to the preparation of heterobimetallics, was obtained (Scheme 1). In addition the intermolecular bis-disulfide of H<sub>2</sub>bme-daco **2** was also isolated and characterized. The latter represents the product of ligand oxidation proposed in one-electron oxidative processes of **Ni-1**,<sup>2</sup> concomitantly releasing Ni<sup>2+</sup> which is rapidly scavenged by **Ni-1**, producing the stable trimetallic species. Its existence supports our supposition that the monomeric intramolecular disulfide of the bme-daco ligand is sterically prohibited, accounting for much of the well behaved S-oxygenation chemistry displayed by the ligand.<sup>3</sup>



**Scheme 1** Synthetic scheme of the reaction of **Ni-1** and PhSeCl.

Compound **1** is, to our knowledge, the only example of a structurally characterized mixed RS–SeR' ligand which is S-bound to a transition metal. Our literature and data base searches find only one other structurally characterized mixed dichalcogenide, a low yield byproduct of an organometallic reaction which is Se-bound, (PhSSePh)Cr(CO)<sub>5</sub>.<sup>4</sup> An interesting bioinorganic reaction of selenocysteine–S-dithiolene coupling at the molybdenum site of *Desulfovibrio desulfuricans* ATCC 27774 formate dehydrogenase (FDH) has implied both Se and S binding at Mo.<sup>5</sup> The following report is a designed mixed dichalcogenide synthesis, doubtlessly made possible by the well known ability of nickel to facilitate the nucleophilicity of thiolate-S as well as to bind charge-neutralized sulfur, stabilizing the RS–SeR' toward disproportionation.

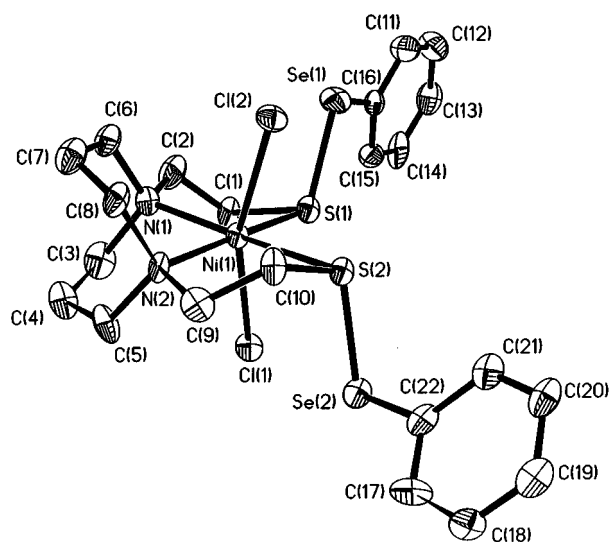
On mixing MeCN solutions of orange PhSeCl with purple **Ni-1**, two different precipitates developed; a major component

was green and the minor, dark red–brown.<sup>6</sup> The mixture was separated by extraction with CH<sub>2</sub>Cl<sub>2</sub> into which the former dissolved. The latter dark solid **3** was identified as a salt of a trimetallic cation<sup>2</sup> (Scheme 1). The green material crystallized in two forms, compounds **1** and **2**, which were characterized by X-ray crystallography. When dissolved in MeOH under Ar, the isolated and purified compound **1**, rapidly disproportionated, producing a mixture of **2**, **3** and diphenyl diselenide (as determined by <sup>1</sup>H NMR).

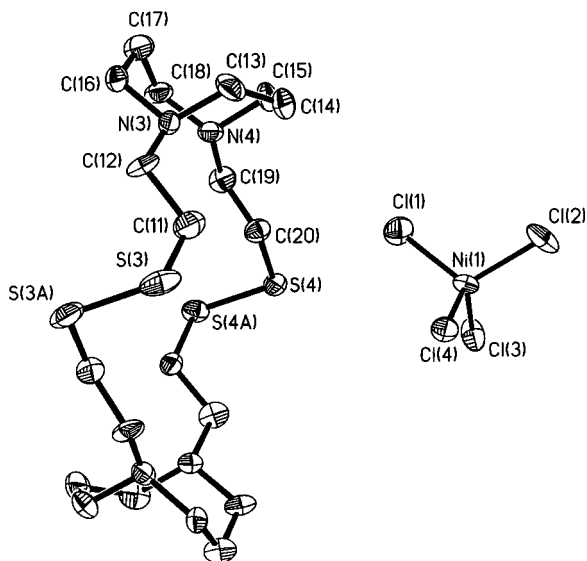
The molecular structures of **1** and **2** are shown in Figs. 1 and 2. Complex **1** contains a pseudo-octahedral nickel in N<sub>2</sub>S<sub>2</sub>Cl<sub>2</sub> coordination; the average deviation in the NiN<sub>2</sub>S<sub>2</sub> best plane is 0.096 Å. The axial chlorides are bent away from the daco framework with a Cl–Ni–Cl angle of 159.07(14)°. As is usual for six-coordinate Ni complexes containing the diazacyclooctane moiety,<sup>7</sup> the fused nickel diazacyclohexane rings adopt chair/chair configurations with the pendant ethylene linkages (NCH<sub>2</sub>CH<sub>2</sub>S) staggered with respect to each other, across the N<sub>2</sub>S<sub>2</sub>Ni plane.

Another open, N<sub>2</sub>S<sub>2</sub> tetradentate, six-coordinate complex based on **Ni-1**,<sup>8</sup> the dibenzyl dibromide complex **4**, is compared to that of **1** in Table 1. Notably, in compound **4** the benzyl groups are on the same side of the N<sub>2</sub>S<sub>2</sub> planes, while the phenylselenolate groups of complex **1** are in *transoid* positions. For both complexes the S–Ni–S angles are *ca.* 10° greater than that of the parent **Ni-1**, corresponding to larger S...S distances (as contrasted to 3.04 Å in **Ni-1**).<sup>7a</sup> The Se–S<sub>av</sub> distance of 2.202(4) Å agrees well with that of Se-bound (CO)<sub>5</sub>Cr(PhS–SePh) ([Se–S = 2.226(6) Å]<sup>4</sup> and the sum of covalent radii of 2.21 Å for a Se–S single bond.<sup>9</sup> The Ph(PhSe)S→Ni dative bond presumably relaxes the typical 90° torsion angle in REE'R dichalcogenides which minimizes lone-pair repulsion. In fact the C–S–Se–CPh torsion angles are 73 and 82°.

A combination of solution conductivity and electrochemical measurements, when compared with previous detailed studies



**Fig. 1** ORTEP drawing (50% probability ellipsoids) of complex **1**. Metric data are given in Table 1.

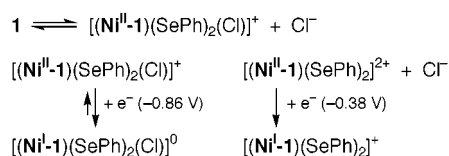


**Fig. 2** ORTEP drawing (50% probability ellipsoids) of complex **2**. Selected distances (Å) and angles (°): S(3)–S(3A) 2.048(7), S(3)–C(11) 1.786(13), S(4)–S(4A) 2.023(6), S(4)–C(20) 1.845(11), av. Ni–Cl 2.272(4); av. Cl–Ni–Cl 107.1(2), C(11)–S(3)–S(3A) 104.0(4), C(20)–S(4)–S(4A) 102.7(4).

**Table 1** Metrical structural data and electrochemical data

Ni–S <sub>av</sub> /Å	2.560(4)	2.493(1)
Ni–N <sub>av</sub> /Å	2.120(11)	2.118(3)
S···S/Å	3.95	3.767
X–Ni–X/°	159.07(14)	162.01(2)
S–Ni–S/°	100.91(12)	98.14(3)
Ni–S–Se(C) <sub>av</sub> /°	109.71(13)	114.91(14)
Reduction potential (Ni <sup>II/I</sup> )/V	–0.38, –0.86	–0.67

of analogues of compound **4** and similar derivatives,<sup>7,8,10</sup> led to the conclusion expressed in Scheme 2. The Ni<sup>II/I</sup> couple at –0.38 V is the most positive observed thus far in a wide range of **Ni-1** thioether dicationic derivatives suggesting that the addition of two SePh<sup>+</sup> groups to the thiolate S achieves a charge neutralization better than that of any carbon-based electrophile. The selenosulfide derivative is less stable to reduction, consistent with weaker S–Se bonds at reduced nickel as compared to S–C bonds.<sup>11</sup> It is also consistent with the observed loss of the Se–S interaction in the reduction of the Mo<sup>VI</sup>-selenosulfide site of FDH<sub>H</sub>.<sup>5</sup> A complicated anodic region of the cyclic voltammogram was not resolved as to ligand or metal-based oxidation.<sup>10,12</sup>



**Scheme 2** The combined results of solution conductivity measurements and electrochemical studies.

The intermolecular disulfide **2** crystallizes in a dicationic protonated form, with NiCl<sub>4</sub><sup>2-</sup> as counter ion. The bisdisulfide attains a cage conformation (C<sub>2</sub> symmetry) with a typical disulfide S–S average distance (2.04 Å) and a large cross cage S(3)···S(4) distance of 7.207 Å. A similar bisdisulfide was isolated as a byproduct of a N<sub>2</sub>S<sub>2</sub> ligating reaction of VOCl<sub>2</sub>(thf)<sub>2</sub>.<sup>13</sup> The H-bonding interaction linking the two N atoms significantly shortens the N···N distance to 2.633 Å, in contrast to **Ni-1**, 2.783 Å.

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## Notes and references

† *Syntheses*: **1** and **2**: At 0 °C, 2 equiv. of PhSeCl (0.150 g, 0.8 mmol) added to a 15 mL CH<sub>3</sub>CN solution of **Ni-1** (0.116 g, 4.0 mmol) produced a green precipitate and a red–brown solid. The resulting mixture was stirred for 30 min, and the solvent was removed *in vacuo*. Extraction of the residue with 20 mL of CH<sub>2</sub>Cl<sub>2</sub> gave a deep green solution. Slow evaporation yielded dark green crystals of **1** and blue–green crystals of **2** in 55 and 3% yield, respectively. **1**: Anal. Calc. (Found) for C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>S<sub>2</sub>NiCl<sub>2</sub>Se<sub>2</sub>: C, 39.20 (39.90); H, 4.49 (4.59); N, 4.16 (4.19)%. UV–VIS(MeOH) λ<sub>max</sub>/nm (ε/M<sup>-1</sup> cm<sup>-1</sup>): 236(3232), 270(937), 316 (272), 338 (145). MS: +ESI; *m/z* (% intensity): 639 (20), 545 (29), 547 (29), 447 (9), 290 (10). <sup>77</sup>Se NMR (CH<sub>2</sub>Cl<sub>2</sub>): δ –372. **2**: Anal. Calc. (Found) for C<sub>20</sub>H<sub>42</sub>N<sub>4</sub>S<sub>4</sub>NiCl<sub>4</sub>: C, 36.00 (36.08); H, 6.34 (5.98)%. MS: +ESI; *m/z* (% intensity): 594 (6), 466 (49), 250 (21), 233 (96), 146 (100).

‡ *Crystal data*: **1**: C<sub>22</sub>H<sub>30</sub>N<sub>2</sub>S<sub>2</sub>NiCl<sub>2</sub>Se<sub>2</sub>, *M* = 674.13, triclinic, space group *P* $\bar{1}$ , *a* = 7.714(2), *b* = 8.031(3), *c* = 22.728(7) Å, α = 81.31, β = 85.50, γ = 65.610(10)°, *U* = 1267.4(7) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.766 g cm<sup>-3</sup>. X-Ray crystallographic data were obtained on a Siemens R3m/V single crystal X-ray diffractometer using Mo–Kα (λ = 0.71073 Å) radiation and equipped with a Siemens LT-2 cryostat. A single crystal was mounted on a glass fiber with epoxy cement at 193(2) K. Structures were solved by direct methods. The elbow carbons C4, C7, C9 and C10 were found to be disordered and were modelled accordingly. Anisotropic refinement for all non-hydrogen atoms was by full-matrix least squares with *R* = 0.0861 and *R*<sub>w</sub> = 0.2187.

**2**: C<sub>20</sub>H<sub>42</sub>Cl<sub>4</sub>N<sub>4</sub>NiS<sub>4</sub>, *M* = 667.33, orthorhombic, space group *Fdd2*, *a* = 27.396(6), *b* = 18.885(4), *c* = 22.838(5) Å, *U* = 11816(4) Å<sup>3</sup>, *Z* = 16, *D*<sub>c</sub> = 1.501 g cm<sup>-3</sup>. X-Ray crystallographic data were obtained on a Siemens R3m/V single crystal X-ray diffractometer using Cu–Kα (λ = 1.54178 Å) radiation and equipped with a Siemens LT-2 cryostat. The structures were solved by direct methods. Anisotropic refinement for all non-hydrogen atoms was by full-matrix least squares with *R* = 0.0569 and *R*<sub>w</sub> = 0.1461. A single crystal was mounted on a glass fiber with epoxy cement at room temperature. CCDC 182/1466.

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