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Monomeric and Dimeric Disulfide Complexes of Nickel(II)

Vlad M. Iluc, Carl A. Laskowski, Carl K. Brozek, Nicole D. Harrold, and Gregory L. Hillhouse*

Department of Chemistry, Gordon Center for Integrative Science, The University of Chicago,
929 East 57th Street, Chicago, Illinois 60637

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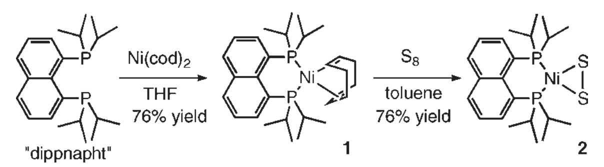
Elemental sulfur reacts with a bulky bis(phosphine)nickel(0) complex to give a monomeric nickel(II) η^2-disulfido complex, oxidation of which results in the elimination of sulfur with dimerization to give an η^2,η^2-disulfidodinickel(II) derivative in which the S−S bond can be reductively cleaved in a redox-reversible fashion.

Scheme 1. Synthesis of **1** and **2**



Nickel complexes containing coordinated dichalcogens, especially sulfur and oxygen, are of interest because of their implication in catalytic oxidations, their intermediacy in desulfurization reactions of chemical feedstocks, and their biorelevance.[1] Disulfur derivatives of nickel can span a range of reduction and activation. Disulfide (S_2^{2-}) ligands on nickel(II) have been crystallographically characterized in three distinct bonding modes: $L_nNi_2(\eta^2,\eta^2\text{-}S_2)$,[2] $L_nNi_2(\mu\text{-}1,2\text{-}S_2)$,[3] and $L_nNi(\eta^2\text{-}S_2)$.[4] Interesting nickel(II) supersulfido (S_2^{-}) complexes (nacnac)Ni(S_2) and {(nacnac)Ni(S_2)}$_2$ [nacnac = CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N}$_2^-$] have recently been reported and exhibit sulfur-ligand-centered radical character.[5] While no terminal sulfido (S^{2-}) complexes of nickel are presently known, Jones has reported the in situ generation of a $L_nNi{=}S$ intermediate that subsequently dimerizes or can be trapped.[6] However, bridging sulfido complexes $LNi_2(\mu\text{-}S)_2$, having no S−S bond (they can be considered as S_2^{4-}, in which the σ^* and both π^* valence molecular orbitals of S_2 are doubly populated), have been described by several groups.[2,6,7] Here we report the synthesis of a monomeric nickel(II) η^2-disulfide complex and its oxidation to a dimeric, bridging nickel(II) η^2,η^2-disulfide with loss of elemental sulfur.

The reaction of 1 equiv of 1,8-bis(diisopropylphosphino)naphthalene (dippnapht)[8] with Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) in a tetrahydrofuran (THF) solution results in the formation of (dippnapht)Ni(cod) (**1**) in 76% yield as yellow-brown crystals (Scheme 1). **1** has been characterized by standard spectroscopic and analytical methods and by single-crystal X-ray diffraction.[9] The ^{1}H NMR spectrum of **1** indicates that a dynamic process involving the cod ligand occurs at room temperature, but its poor solubility at lower temperatures in common solvents has prevented elucidation of this process by variable-temperature (VT) NMR experiments.

The addition of 1 equiv of S_8 to a toluene solution of **1** results in the oxidation of nickel to give a monomeric η^2-disulfide complex, (dippnapht)Ni(η^2-S_2) (**2**), as analytically pure orange crystals in 76% isolated yield (Scheme 1). The solid-state structure of **2** (Figure 1) reveals a four-coordinate, planar nickel center with S(1)−S(2) = 2.059(2) Å and Ni−S distances of 2.204(3) and 2.185(3) Å. These are comparable to the S−S [2.038(5) Å] and Ni−S [2.178(4) and 2.193(4) Å] distances observed for the S_2^{2-} ligand in $[S_2W(\mu\text{-}S)_2Ni(\eta^2\text{-}S_2)][PPh_4]_2$,[4] the only other structurally characterized complex containing a nonbridging Ni(η^2-S_2) moiety. As expected, the S(1)−S(2) distance in **2** is ~0.1 Å longer than the corresponding distance in the supersulfido (S_2^{-}) complex {(nacnac)Ni(S_2)}$_2$ [1.944(2) Å].[5]

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*To whom correspondence should be addressed. E-mail: g-hillhouse@uchicago.edu.

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[9] See the Supporting Information for crystallographic details for **1**.

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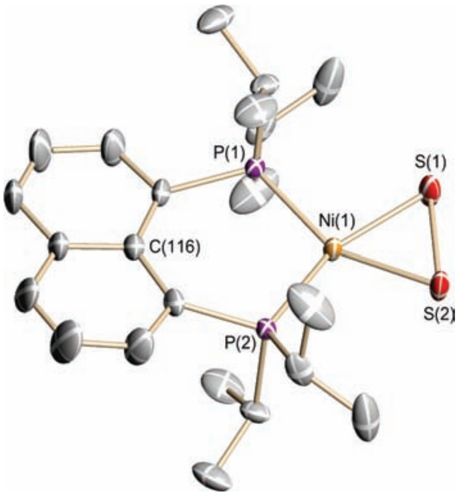
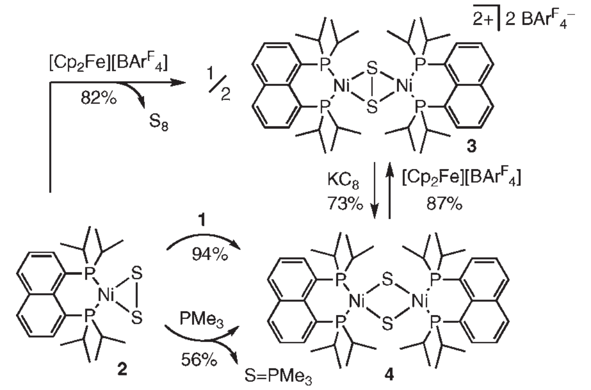


Figure 1. X-ray structure of **2** (50% probability). H atoms are omitted for clarity. Selected metrical parameters (distances in angstroms and angles in degrees): S(1)−S(2) = 2.059(2), Ni(1)−S(1) = 2.204(3), Ni(1)−S(2) = 2.185(3); S(1)−Ni(1)−S(2) = 55.97(6), P(1)−Ni(1)−P(2) = 98.89(5), P(1)−Ni(1)−S(1) = 102.98(7), P(2)−Ni−S(2) = 102.23(8), Ni(1)−S(1)−S(2) = 61.56(14), Ni(1)−S(2)−S(1) = 62.47(13).

Scheme 2. Redox Processes That Interconvert Complexes **2**−**4** Involve the Sulfur Ligands, not the Nickel(II) Centers



The reaction of a THF solution of **2** with 1 equiv of $[Cp_2Fe][BAr^F_4]$ ($BAr^F_4 = B[3,5-(CF_3)_2C_6H_3)]_4$) results in the formation of the dicationic dimer, $[\{(\text{dippnapht})Ni\}_2(\eta^2{:}\eta^2-S_2)][BAr^F_4]_2$ (**3**), as a dark-red, analytically pure solid in 82% yield (Scheme 2). Gas chromatography/mass spectrometry analysis of the reaction solution indicates that the fate of the second S_2 moiety is in the formation of S_8 (M + 256). Thus, oxidation of **2** results in the two-electron oxidation of the S_2^{2-} subunit instead of nickel, formally giving sulfur and "(dippnapht)Ni^{2+}", which reacts via dimerization with **2** to give **3**. Attempts to trap the eliminated S_2 with 2,3-dimethyl-1,3-butadiene resulted in the detection of primarily S_8, with only a minor component of the expected Diels−Alder product (< 2%) observed.[10]

Complex **3** is diamagnetic and has been characterized by solution NMR spectroscopy, X-ray diffraction, and elemental analysis. The solid-state structure of **3** shows a puckered, butterfly-like geometry for the Ni_2S_2 kernel (the two NiS_2 planes' torsion angle = 112.2°) with planar, four-coordinate d^8 nickel centers flanking the central S_2^{2-} unit (Figure 2). The Ni atoms are well separated at 3.2326(4) Å. The Ni−S [2.197(2) and 2.202(2) Å] and S(1)−S(2) [2.054(2) Å] distances in **3** are similar to those found in **2** and in the related neutral, butterfly-shaped complex $\{(\text{nacnac})Ni\}_2(\eta^2{:}\eta^2-S_2)$ [with S−S = 2.051(1) Å and Ni_2S_2 = 133.9°].[5]

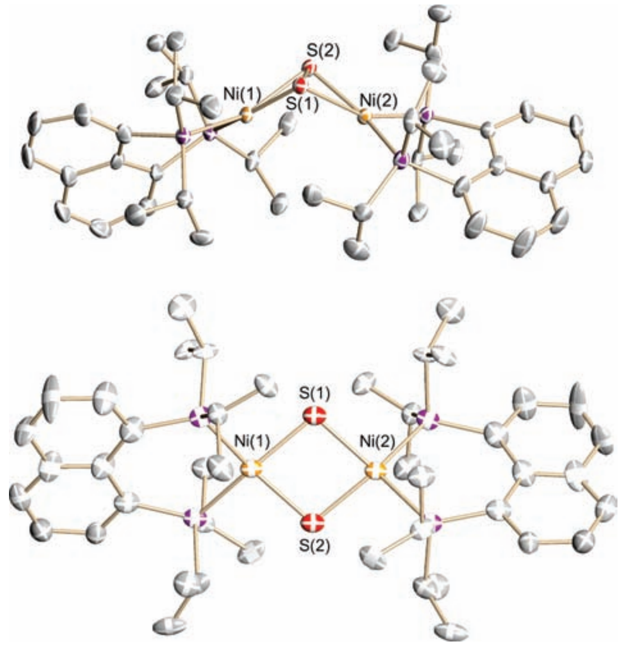


Figure 2. X-ray stuctures of the complex dications of **3** (top) and **4** (bottom) (50% probability), H atoms and BAr^F_4 counterions are omitted for clarity. Selected metrical parameters (distances in angstroms and angles in degrees) for **3**: S(1)−S(2) = 2.054(2), Ni(1)−S(1) = 2.197(2), Ni(1)−S(2) = 2.202(2), Ni(1)−Ni(2) = 3.2326(4); Ni(1)−S(1)−Ni(2) = 94.35(6), Ni(1)−S(2)−Ni(2) = 94.60(6), S(1)−Ni(1)−S(2) = 55.66(5), S(1)−Ni(2)−S(2) = 55.57(5). Those for **4**: S(1)−S(2) = 2.839(4), Ni(1)−S(1) = 2.165(4), Ni(1)−S(2) = 2.176(4), Ni(1)−Ni(2) = 3.284(2); Ni(1)−S(1)−Ni(2) = 98.6(2), Ni(1)−S(2)−Ni(2) = 98.0(2), S(1)−Ni(1)−S(2) = 81.7(2).

The reduction of solutions of **3** with potassium graphite yields the neutral bis(μ-sulfido)nickel(II) dimer $\{(\text{dippnapht})Ni\}_2(\mu-S)_2$ (**4**) as a diamagnetic brown solid in 72% isolated yield (Scheme 2). The reduction occurs at the S_2^{2-} ligand to give two μ-S^{2-} ligands, with nickel remaining in the 2+ oxidation state.

The solid-state structure of **4** is shown in Figure 2 and reveals a long S(1)−S(2) separation [2.839(4) Å] consistent with the reduction of the S_2^{2-} ligand to S_2^{4-} and cleavage of the remaining S−S σ bond (Figure 2). Unlike in **3**, the Ni and S atoms of **4** are rigorously coplanar. This reduction is reversible, and the reaction of **4** with $[Cp_2Fe][BAr^F_4]$ results in its oxidation to **3** in high yield (Scheme 2). Complex **4** can be independently synthesized by alternative methods (Scheme 2). The reaction of **1** and **2** in a 1:1 stoichiometry gives **4** in high yield. In this reaction, the nickel(0) reagent **1** reduces the S_2^{2-} unit in **2** by two electrons, giving the observed $Ni^{II}-Ni^{II}$ product. Consistent with this finding, the reaction of carefully controlled, stoichiometric amounts of S_8 (Ni:S = 1:1) with **1** gives **4** directly, presumably via the intermediacy of **2**. A third route to **4** involves thermolysis of **2** with an excess of PMe_3, resulting in the formation of $S{=}PMe_3$ and **4** in moderate yield.[11] We observed no spectroscopic evidence for a (dippnapht)Ni=S intermediate,

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although such a monomeric sulfido complex seems to be a logical precursor to **4** in this reaction.[12]

In summary, the use of a bulky, naphthalene-based bis(phosphine) has allowed for isolation of a monomeric nickel(II) η^2-disulfide complex (**2**), which can be cleanly oxidized with ferrocenium to generate a dicationic S_2^{2-} bridging disulfide dimer (**3**) with elimination of elemental sulfur. The dimer **3** undergoes clean and reversible reduction to a new neutral dimer (**4**) in which reduction takes place within the S_2 unit and results in cleavage of the S−S bond. The dimer **4** can be prepared from other routes, but no evidence is found for a stable terminal sulfido complex in this system.

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Supporting Information Available: Experimental, spectroscopic, and analytical details and complete crystallographic details for **1**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Dimer **4** can also be prepared by the reaction of (dippnapht)NiCl with $LiSPh_3$. Gomberg's dimer was also observed as a product. The mechanism of this reaction, involving the elimination of $Ph_3C^\bullet$, also implicates a (dippnahpt)Ni=S intermediate.