

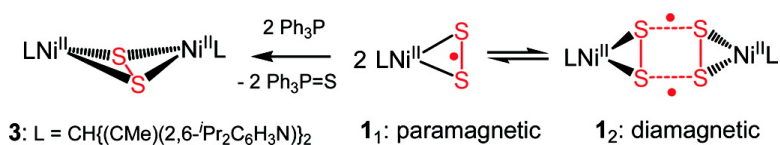
Communication

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From a Paramagnetic, Mononuclear Supersulfidonickel(II) Complex to a Diamagnetic Dimer with a Four-Sulfur Two-Electron Bond

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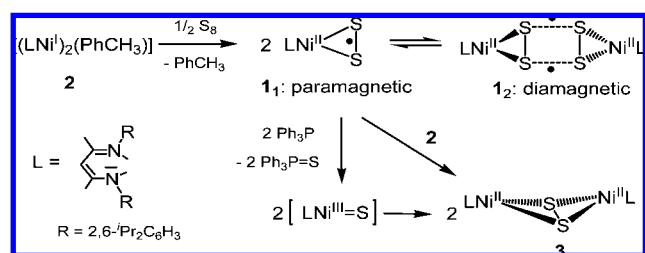
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Transition-metal complexes of diatomic chalcogen ligands X_2 are of interest because of their role in oxidation processes in biological and catalytic systems.¹ Owing to their importance, respective peroxy (O_2^{2-}) as well as persulfido (disulfido) complexes (S_2^{2-}) have attracted much attention, resulting in a vast number of complexes for structure–reactivity studies containing one or more X_2 units with a “side-on” or “end-on” coordination mode.² In contrast, much less is known about complexes containing the paramagnetic superoxo (O_2^-) and supersulfido (S_2^-) ligand, respectively, despite the fact that they can be key intermediates in metal-mediated X–X bond activation and X–atom transfer reactions.^{3,4} Thus it is challenging in synthetic chemistry to develop isolable superchalcogenidometal complexes capable of soft X–atom transfer for chemoselective C–H bond functionalization. Up to now, the elusive S_2^- radical anion could only be detected by spectroscopy^{5a} and only a few “end-on” supersulfido complexes have been characterized structurally.^{4,5b,c} A “side-on” supersulfido complex is as yet unknown. Recently, we developed a simple route to the first isolable superoxonickel complex $[LNi(O_2)]$ bearing a tetracoordinate Ni(II) center by taking advantage of the electronic nature of the bulky substituted, monoanionic β -diketiminato ligand L^- , $CH\{(CMe)(2,6\text{-}i\text{-}Pr_2C_6H_3N)\}_2^-$.⁶ The latter complex results from one-electron reduction of O_2 by the corresponding Ni(I) precursor. Its fascinating magnetic properties and reactivity prompted us to probe whether the supersulfidonickel homologue **1** could be synthesized by direct oxidation of the same Ni(I) precursor, $[LNi](\text{toluene})$ **2**, with elemental sulfur. Herein, we report the facile synthesis, the striking structural features, and the reactivity of the first supersulfidonickel complex **1** with the “side-on” S_2^- ligand.

Reaction of **2** with S_8 in a molar ratio of 2:1 in toluene at -60°C slowly gives rise to a color change from red-brown to yellow-brown. The complete conversion of **2** to **1** can be ensured by warming up the mixture to room temperature (Scheme 1).

Scheme 1. Synthesis of **1** and **3**



Recrystallization of the crude product from *n*-hexane solutions at -20°C affords dark brown, air-stable crystals of **1** in 87% yield. Its composition is proven by elemental analysis (C, H, N, S) and

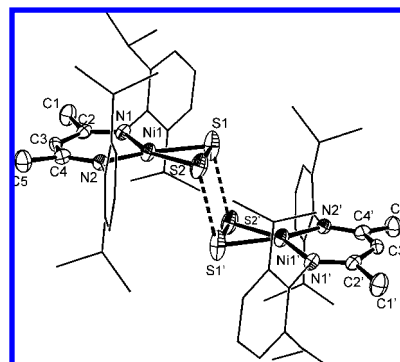


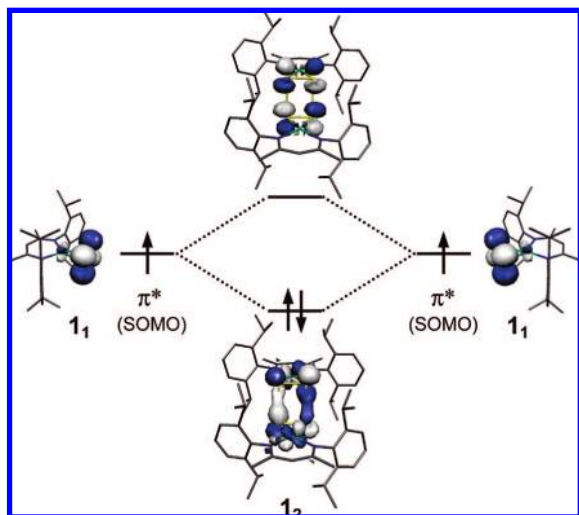
Figure 1. Molecular structure of **1**₂ in the crystal. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. (Atoms with a prime (') have equivalent coordinates $(-x + 2, -y + 1, -z)$. For details see Supporting Information.

EI mass spectrometry. Its molecular structure has been established by X-ray diffraction analysis (Figure 1). Unexpectedly, the compound crystallizes in the form of centrosymmetric dimers (**1**₂) featuring a four-membered, rectangular-shaped S_4 ring with two relatively short (S1–S2 194.4(2) pm) and two very long S–S distances (S1–S2' 277.7(2) pm). The S1–S2 distance is significantly shorter than that in $[(S_2WS_2)Ni(S_2)]^{2-}$ (203.8 pm),^{7a} and those values observed in related “side-on” disulfido complexes.^{1a} Likewise, the S1–S2 distance is only slightly longer than the value for the S=S double bond in S_2 (189 pm) and in $[S_2I_4]^{2+}$ (182 pm)^{7b} indicating significant double-bond character of the supersulfido S_2^- ligand. This is consistent with the $\nu(S-S)$ stretching vibration mode of 606 cm^{-1} determined by IR spectroscopy.^{2c} The much longer S1–S2' distance is substantially smaller than the sum of the van der Waals radii (360 pm) and even shorter than the transannular S–S distance in S_8^{2+} (288 pm)^{8a} but similar to those in metal complexes with a rectangular S_4 unit.^{8b} How could one explain this peculiar association? Since **1**₁ is isolobal with its paramagnetic superoxo homologue,⁶ the SOMO of which is a singly occupied π^* orbital that is completely localized on the O_2 ligand, the dimerization of **1**₁ leads to a stabilization by $\pi^*-\pi^*$ interaction between the larger sulfur atoms. This is supported by DFT calculations (see below and Supporting Information). Accordingly, the measurement of the effective magnetic moment of a solid sample of **1**₂ displays diamagnetic behavior. Apparently, the driving force for the dimerization arises from the formation of a four-sulfur two-electron bond. As expected, the geometric features of the $LNiS_2$ subunit are identical to those of the oxygen homologue, consisting of an almost planar six-membered C_3N_2Ni ring and a square-planar, tetracoordinate low-spin Ni(II) atom. The Ni–S distances of 216.3(1) and 216.6(1) pm are close to those values in $[(S_2WS_2)Ni(S_2)]^{2-}$ (av 218.6 pm),^{7a} but significantly shorter than those values in a

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Scheme 2. Orbital Diagram for the Dimerization of **1**₁ via $\pi^*(\text{SOMO})-\pi^*(\text{SOMO})$ Interaction with a Four-Sulfur Two-Electron Bond in the Dimer **1**₂



dinuclear, butterfly like Ni(II) disulfido complex with a $\text{Ni}_2(\mu-\eta^2:\eta^2-\text{S}_2)$ core [224.2(1) and 224.8(1) pm],^{9a} and in related diphosphinonickel(II) disulfides.^{9c} Apparently, diamagnetic **1**₂ dissociates in *d*₆-benzene solutions at ambient temperature to paramagnetic **1**₁ as indicated by its ¹H NMR spectrum displaying paramagnetically shifted resonances similar to its oxygen homologue. X-band EPR measurements of **1** in toluene solutions at room temperature reveal a paramagnetic ground-state for **1**₁ with spin $S = 1/2$. The spectrum in frozen solution at 50 K is rhombic and has principal *g* values of 2.148, 2.082, and 2.073. The corresponding average value, $g_{\text{av}} = 2.101$, resembles that of S_2^{2-} in NaI.^{5a} Since the intensity of the low temperature spectrum reveals less than 5% spin concentration, **1**₁ and **1**₂ must be present in a thermal equilibrium, and predominantly diamagnetic dimers **1**₂ have been trapped upon freezing of the toluene solutions.

Density functional theory (DFT) calculation of monomeric **1**₁ reveals that the HOMO is a singly occupied π^* -orbital (SOMO) completely located on the S₂ ligand, indicating that the molecule is a genuine supersulfido complex. Single point calculations of the electronic structure of **1**₂ based on the X-ray structure prove that the dimer results from $\pi^*(\text{SOMO})-\pi^*(\text{SOMO})$ interaction, leading to a four-sulfur two-electron bond (Scheme 2). This bonding situation is similar to that in a diphosphirenyl dimer with a four-phosphorus two-electron bond previously reported by Bertrand et al.¹⁰

Although **1**₁ and its oxygen homologue seem electronically very similar, they lead to very different products by gentle dechalcogenation with Ph₃P. While the superoxonickel homologue reacts with Ph₃P to give Ph₃PO and an unusual dinuclear $[\text{Ni}^{\text{II}}_2(\mu-\text{OH})_2]$ complex with tetrahedral and square-planar Ni(II) sites,⁶ sulfur transfer from **1** to Ph₃P furnishes Ph₃PS and the corresponding dinuclear, butterfly like $[\text{Ni}^{\text{II}}_2(\mu-\eta^2:\eta^2-\text{S}_2)]$ complex **3** in quantitative yield (Scheme 1). Alternatively, the reaction of **1** and **2** (1:1 molar ratio) leads also exclusively to the formation of **3**, which has been isolated as black crystals and fully characterized. Since **3** is a genuine disulfido complex, the compound is diamagnetic and displays two chemically equivalent β -diketiminato ligands in its ¹H NMR spectrum. Complex **3** consists of a puckered Ni₂S₂ core (dihedral angle between the two NiS₂ planes: 133.9°) with almost square-planar, tetracoordinate Ni(II) atoms (Figure 2). The S1–S2

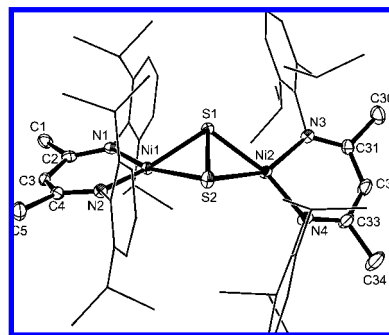


Figure 2. Molecular structure of compound **3**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity. For details see Supporting Information.

bond distance of 205.1(1) pm is longer than that in **1**₂, but shorter than those observed in other complexes with a $\text{Ni}_2(\mu-\eta^2:\eta^2-\text{S}_2)$ core [ranging from 217.7(2) to 229.7(4) pm].^{9a-d} The shorter S–S distance in **3** indicates a less activated S–S bond in the S₂²⁻ bridge owing to a smaller back-donation by the Ni centers compared to those disulfido nickel complexes with higher coordination number (>4) on nickel.^{9a}

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Supporting Information Available: Experimental details for the synthesis and spectroscopic data of **1** and **3**, DFT calculations, and Cartesian coordinates of **1**₁ and **1**₂; crystallographic data for **1**₂ and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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