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Synthesis of a “Masked” Terminal Nickel(II) Sulfide by Reductive Deprotection and its Reaction with Nitrous Oxide

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***Abstract:** The addition of 1 equiv of $KSCPh_3$ to $[L^RNiCl]$ ($L^R = \{(2,6\text{-}iPr_2C_6H_3)NC(R)\}_2CH$; R = Me, tBu) in C_6H_6 results in the formation of $[L^RNi(SCPh_3)]$ (**1**: R = Me; **2**: R = tBu) in good yields. Subsequent reduction of **1** and **2** with 2 equiv of KC_8 in cold (−25 °C) Et_2O in the presence of 2 equiv of 18-crown-6 results in the formation of “masked” terminal Ni^{II} sulfides, $[K(18\text{-crown-}6)][L^RNi(S)]$ (**3**: R = Me; **4**: R = tBu), also in good yields. An X-ray crystallographic analysis of these complexes suggests that they feature partial multiple-bond character in their Ni–S linkages. Addition of N_2O to a toluene solution of **4** provides $[K(18\text{-crown-}6)][L^{tBu}Ni(SN{=}NO)]$, which features the first example of a thiohyponitrite (κ^2-$[SN{=}NO]^{2-}$) ligand.*

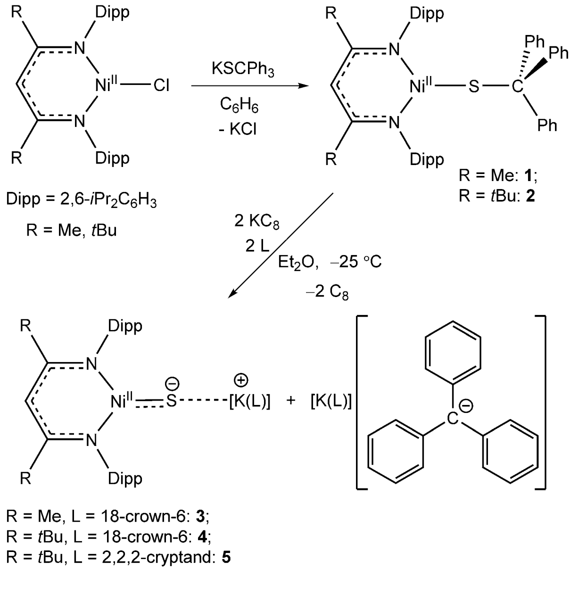
Metal–ligand multiple bonding in the late transition metals (Groups 9, 10, 11) is relatively rare.[1,2] This observation can be rationalized by the “oxo wall” concept,[3] which postulates that a tetragonal complex with d^5 configuration (or greater) cannot form stable multiple bonds because of occupation of the M=E π* orbitals. Whereas no exceptions to the “oxo wall” concept are currently known, it can be circumvented by reducing the coordination number at the metal center. For example, two late-metal oxo complexes have been reported, namely $[Ir(O)(Mes)_3]$ (Mes = 2,4,6-$Me_3C_6H_2$) and [Pt(O)-(PCN)] (PCN = $C_6H_3[CH_2P(tBu)_2](CH_2CH_2NMe_2)$), and both feature four-coordinate geometries.[4,5] Two recently isolated Ir nitride complexes also feature four-coordinate geometries.[6,7] Similarly, a handful of isolable cobalt, nickel, and copper nitrene species are known, for example $[(Me_2NN)Co(NAd)]$ ($Me_2NN = \{(2,6\text{-}Me_2C_6H_3)NC(Me)\}_2CH$), $[(dtbpe)Ni(N(2,6\text{-}iPr_2C_6H_3))]$ (dtbpe = $tBu_2PCH_2CH_2PtBu_2$), $[(IPr^*)Ni(N(2,6\text{-}(Mes)_2C_6H_3))]$, and $[\{(Me_3NN)Cu\}_2(\mu\text{-}NAd)]$ ($Me_3NN = \{(2,4,6\text{-}Me_3C_6H_2)NC(Me)\}_2CH$), which also feature low coordination numbers (2–4).[8–11] Also of note are the closely related nickel carbene and phosphinidene complexes [(dtbpe)Ni(E)] (E = CPh_2, $P(2,6\text{-}(Mes)_2C_6H_3)$), reported by Hillhouse and co-workers.[12,13] This class of materials is highly reactive and capable of effecting CO oxidation, C–H activation, and [2+2] cycloaddition, demonstrating their utility for small-molecule activation.[14–25]

In contrast to the above-mentioned success with C, O, N, and P donor multiple bonds, attempts to synthesize a stable late-metal terminal sulfide have been unsuccessful. For example, Driess and co-workers postulated that reaction of $[L^RNi(\eta^2\text{-}S_2)]$ ($L^R = \{(2,6\text{-}iPr_2C_6H_3)NC(Me)\}_2CH$ with Ph_3P resulted in transient formation of $[L^RNi(S)]$, which, however, rapidly dimerizes to form a bridged disulfide complex.[26] Similarly, Jones and Vicic reported the transient formation of [(dippe)Ni(S)], which could be trapped by a variety of nitrones.[27]

Recently, we reported the synthesis of a Th^{IV} sulfide complex, $[K(18\text{-crown-}6)][Th(S)(NR_2)_3]$ (R = $SiMe_3$), by reductive removal of the trityl protecting group.[28] Building on this work, we next attempted to apply this “reductive deprotection” reaction to the synthesis of an isolable late-metal terminal sulfide. Herein, we report the synthesis of a “masked” terminal Ni^{II} sulfide and describe its reactivity with nitrous oxide.

Addition of 1 equiv of $KSCPh_3$ to $[L^RNiCl]$ (R = Me, tBu)[29] in C_6H_6 results in the formation of $[L^RNi(SCPh_3)]$ (**1**: R = Me; **2**: R = tBu; Scheme 1). Their formulations were confirmed by elemental analysis and X-ray crystallography (full structural details can be found in the Supporting Information). Moreover, their ^1H NMR spectra are similar to those reported for other Ni^{II} β-diketiminate thiolate complexes, such as $[L^{tBu}Ni(SPh)]$ and $[L^{tBu}Ni(SEt)]$.[30,31]

Subsequent reduction of **1** and **2** with 2 equiv of KC_8 in cold (−25 °C) Et_2O in the presence of 2 equiv of 18-crown-6



Scheme 1. Syntheses of complexes **1**–**5**.

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results in the formation of [K(18-crown-6)][L^{R}Ni(S)] (**3**: R = Me; **4**: R = *t*Bu). Complex **3** could be isolated as dark green blocks from hexanes/C_6H_6 in 66 % yield, whereas complex **4** was isolated as dark brown plates from toluene/isooctane in 88 % yield. Similarly, use of 2,2,2-cryptand in place of 18-crown-6 afforded [K(2,2,2-cryptand)][L^{tBu}Ni(S)] (**5**), which was isolated as brown needles in 89 % yield after crystallization from hexanes. The syntheses of **3**, **4**, and **5** also produce 1 equiv of [K(L)][CPh_3] (L = 18-crown-6, 2,2,2-cryptand), which precipitates from the reaction mixtures as a bright red solid that can be separated from the nickel-containing products by filtration (Scheme 1). Interestingly, C–S bond cleavage has previously been observed in a Ni tritylthiolate complex.[32] For example, Riordan and co-workers reported the formation of [{PhB(CH_2S*t*Bu)$_3$}Ni]$_2$(μ_2-η^2,η^2-S_2) and ${}^{\bullet}CPh_3$ upon thermal decomposition of [{PhB(CH_2S*t*Bu)$_3$}Ni-($SCPh_3$)]; however, there was no evidence for the generation of a terminal sulfide in this reaction.

The formulations of complexes **3**, **4**, and **5** were confirmed through elemental analysis, ^{1}H NMR spectroscopy, and X-ray crystallography. The solid-state structures of **4** and **5** are shown in Figure 1, and selected metrical parameters can be found in Table 1. Complexes **3**, **4**, and **5** feature identical coordination environments about their Ni centers. In the solid state, each exhibits a planar (Σ(L-Ni-L) ≈ 360°), Y-shaped geometry. The Ni–S bond lengths in **3**–**5** range from 2.0635(6) to 2.084(1) Å. All three complexes feature long S–K interactions,[28,33] which range from 3.094(2) to 3.379(1) Å. Not surprisingly, complex **5**, which features the strongest K$^+$ chelator (2,2,2-cryptand), exhibits the longest S–K interaction. Interestingly, the Ni-S-K angles vary widely, from 153.74(3)° (for **3**) to 177.95(8)° (for **4**), a disparity that we ascribe to crystal packing. Furthermore, complex **4** exists as a dimer in the solid state; its monomer units are connected by bridging interactions between the [K(18-crown-6)]$^+$ cations (Figure 1). Finally, the Ni–N distances in **3**–**5** are comparable to those found in other three-coordinate Ni^{II} β-diketiminate complexes.[29–31,34]

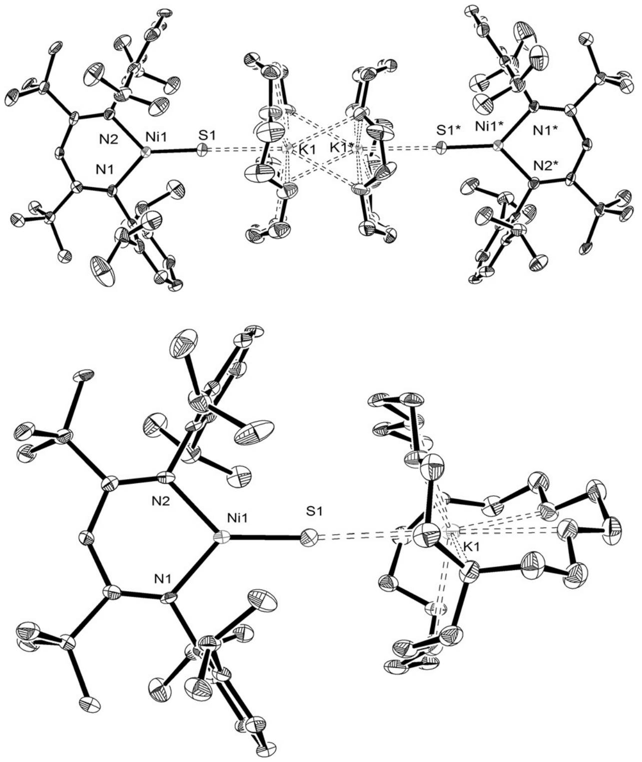


Figure 1. ORTEP drawings of [K(18-crown-6)][L^{tBu}Ni(S)] (**4**·C_8H_{18}; top) and [K(2,2,2-cryptand)][L^{tBu}Ni(S)] (**5**, bottom). Thermal ellipsoids shown at 50% probability. Hydrogen atoms and C_8H_{18} solvate molecules have been omitted for clarity.

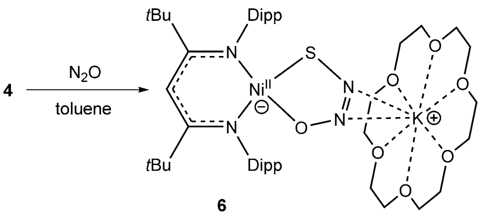
Table 1: Selected bond lengths and angles for the nickel(II) sulfide complexes **3**, **4**, and **5**.

Bond/angle	3	4	5
Ni1–S1 [Å]	2.0635(6)	2.064(2)	2.084(1)
S1–K1 [Å]	3.1212(7)	3.094(1)	3.379(1)
Ni–N (av.) [Å]	1.94	1.93	1.93
Ni1-S1-K1 [°]	153.74(3)	177.95(8)	170.08(5)

The Ni–S bond lengths in complexes **3**, **4**, and **5** are amongst the shortest known, and are intermediate between the additive covalent radii projected for nickel–sulfur single (2.13 Å) and double bonds (1.95 Å).[23,24,35] For comparison, [{L^{tBu}Ni}$_2$(μ-S)],[30] [{(IPr)Ni}$_2$(μ-S)$_2$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[36] and [{PhB-(CH_2S*t*Bu)$_3$}Ni]$_2$(μ-S)[32] display comparable Ni–S bond lengths of 2.0651(7), 2.0972(6), and 2.0714(4) Å, respectively, despite each possessing a bridging S^{2-} ligand. Overall, this suggests similar magnitudes of π-bonding in both classes of materials.

The ^{1}H NMR spectra of complexes **3**–**5** in C_6D_6 are typical of three-coordinate, high-spin Ni^{II} β-diketiminate complexes.[29,34] Notably, the resonances assignable to the [K(18-crown-6)]$^+$ cations are broad and shifted to 1.18 and 0.28 ppm for **3** and **4**, respectively. The 2,2,2-cryptand resonances for **5** are similarly broadened and shifted. These data suggest that the [K(L)]$^+$ cations form a contact pair with the [L^{R}Ni(S)]$^-$ anions in solution. In the solid state, complexes **3** and **4** exhibit effective magnetic moments of 2.80 B.M. at 300 K (D = 91 cm^{-1}) and 2.98 B.M. at 300 K (D = 94 cm^{-1}), respectively (Figures S22, S23). This behavior is consistent with that anticipated for a Y-shaped Ni^{II} complex with an S = 1 ground state.[37] Overall, the solid-state molecular structures and magnetic properties of **3**–**5** confirm our Ni^{II} oxidation-state assignments, and exclude the possibility that the sulfur atom is protonated, as this would require nickel to be in the +1 oxidation state. Intriguingly, the related Ni^{II} imido, carbene, and phosphinidene complexes, such as [(dtbpe)Ni(E)], are diamagnetic.[9,12,13] This change in spin state may reflect different amounts of π-bonding in the two classes of molecules.

The combined characterization data for complexes **3**–**5** reveal that the S–K interaction is conserved in both solution and the solid state. However, preliminary reactivity data suggest that the S–K interaction is quite labile, permitting these complexes to behave as "masked" terminal sulfides.[38] For example, exposure of complex **4** to an atmosphere of nitrous oxide (N_2O) resulted in a rapid color change from dark brown to yellow. Isolation of the resulting product by crystallization from toluene/isooctane provided [K(18-crown-6)][L^{tBu}Ni(SN=NO)] (**6**) as an orange crystalline solid in 62% yield [Eq. (1)]. Complex **6** crystallized in the triclinic space group $P\bar{1}$, and its solid-state molecular structure is shown in Figure 2. Complex **6** features an unprecedented κ^2-thiohyponitrite ($[SN{=}NO]^{2-}$) ligand, formed by [3+2] cycloaddition of N_2O across the Ni–S bond. The S–N and O–N distances in the $[SN{=}NO]^{2-}$ moiety are 1.787(6) Å and 1.308(1) Å, respectively, and are suggestive of single bonds, while the N–N bond length of 1.154(9) Å is indicative of a double bond. These parameters are consistent with the presence of a dianionic hyponitrite moiety, which, in combination with the diamagnetism of **6**, as revealed by its ^{1}H NMR spectrum (see the Supporting Information), is consistent with the anticipated Ni^{II} oxidation state.



6 (1)

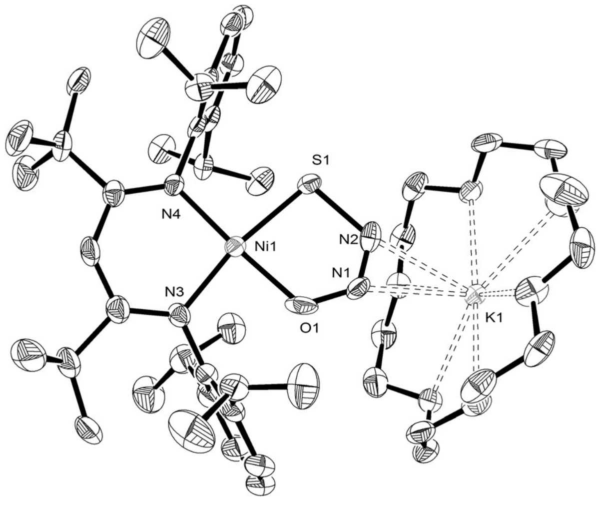


Figure 2. ORTEP drawing of [K(18-crown-6)][L^{tBu}Ni(κ^2-SN=NO)] (**6**·1.5 C_7H_8·0.5 C_8H_{18}). Thermal ellipsoids shown at 50% probability. Hydrogen atoms and C_7H_8 and C_8H_{18} solvate molecules have been omitted for clarity.

Complex **6** is a rare example of a structurally characterized transition-metal complex containing activated N_2O and features the first example of a thiohyponitrite (κ^2-$[SN{=}NO]^{2-}$) ligand. Its formation is reminiscent of the frustrated Lewis pair (FLP) systems $tBu_3P/B(C_6F_5)_3$ and $[\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(B(C_6F_5)_2)]$, which react with N_2O to form $[tBu_3P(N{=}NO)B(C_6F_5)_3]$[39] and $[\{(C_6H_4)_2(O)CMe_2\}(PMes_2)(N{=}NO)(B(C_6F_5)_2)]$,[40] respectively, or the reaction of N_2O with Na_2O, which results in the formation of *trans*-$[Na_2N_2O_2]$.[41,42] Also relevant is the reaction of IPr with N_2O to form IPr–N_2O.[43] These results support the conclusion that the $[SN{=}NO]^{2-}$ ligand is formed by nucleophilic attack of N_2O at the sulfide ligand in **4**.[39,43,44]

In summary, cleavage of the C–S bond in [L^RNi(SCPh$_3$)] by reductive deprotection provides access to a family of "masked" terminal Ni^{II} sulfides, [K(L)][(L^R)Ni(S)]. The Ni–S distances in this class of materials are amongst the shortest observed, suggesting the presence of partial multiple-bond character. [K(18-crown-6)][(L^{tBu})Ni(S)] reacts with N_2O to form a novel thiohyponitrite complex, [K(18-crown-6)][L^{tBu}Ni(SN=NO)], confirming the lability of the S–K interaction. Going forward, we will continue to explore the small-molecule reactivity of this class of complexes. Furthermore, we will target the synthesis of their oxygen congeners.

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Keywords: coordination chemistry · nickel · nitrogen oxides · protecting groups · sulfides

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