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Activation of CS_2 by a “Masked” Terminal Nickel Sulfide

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The “masked” terminal nickel sulfide complexes [K(L)][(L^{tBu})Ni^{II}(S)] (L^{tBu} = {(2,6-$^{i}Pr_2C_6H_3$)NC(^{t}Bu)}$_2$CH, L = 18-crown-6, 2,2,2-cryptand) activate CS_2 to give the trithiocarbonate products [(L^{tBu})Ni^{II}(*S,S*:κ$_2$-CS_3)]$^-$ or [(*S,S*:κ$_2$-CS_3)Ni^{II}{*S,S*:κ$_2$-CS_2(L^{tBu})}]$^-$, further confirming the nucleophilicity of the sulfide (S^{2-}) ligand in these complexes.

There are now a number of reports on the synthesis and reactivity of late transition metal (groups 9, 10, and 11) complexes containing terminal imido (NR^{2-}), phosphido (PR^{2-}), and carbene (CR_2^{2-}) ligands.[1-12] In contrast, the synthesis and reactivity of late transition metal complexes containing terminal chalcogenide ligands (O, S, Se, Te) remains largely unexplored. This is due, in part, to the paucity of this class of materials. Only a handful of late metal oxo complexes have been reported,[13, 14] including the Pt^{IV} terminal oxo (O^{2-}) complex, [Pt(O)(PCN)][BF_4] (PCN = C_6H_3[CH_2P(*t*Bu)$_2$]($CH_2CH_2NMe_2$)), which can perform inter- and intramolecular electrophilic O-atom transfer. Similarly, we recently reported the synthesis and structure of the “masked“ terminal nickel sulfides, namely [K(L)][(L^{tBu})Ni^{II}(S)] (L^{tBu} = {(2,6-$^{i}Pr_2C_6H_3$)NC(^{t}Bu)}$_2$CH, L = 18-crown-6, 2,2,2-cryptand). Preliminary reactivity studies suggest that the sulfide ligand in these comlpexes is quite nucleophilic. For example, [K(18-crown-6)][(L^{tBu})Ni^{II}(S)] readily activates nitrous oxide (N_2O), via nucleophilic attack, to form a novel thiohyponitrite ($SN{=}NO^{2-}$) complex.[15] Herein, we describe the reactions of carbon disulfide (CS_2) with the sulfide ligand of [(L^{tBu})Ni^{II}(S)]$^-$ in an effort to further probe the reactivity of late metal sulfides.

Treatment of [K(18-crown-6)][(L^{tBu})Ni^{II}(S)] with one equivalent of CS_2 in toluene affords a yellow-orange solution from which orange plates of [K(18-crown-6)][(L^{tBu})Ni^{II}(*S,S*:κ$_2$-CS_3)] (**1**) could be isolated in 76% yield (Scheme 1). Complex **1** was shown by X-ray crystallography to contain a bidentate trithiocarbonate (CS_3^{2-}) ligand coordinated to nickel (Figure 1). In the solid state, the Ni^{II} ion features a square planar (Σ(L-Ni-L) = 360°) coordination environment with Ni-N and Ni-S bond lengths that are typical of Ni^{II}.[15-19] The C-S bond lengths in **1** (C-S = 1.666(4), 1.697(4), 1.696(4) Å) are intermediate between C-S single and double bonds, consistent with a trithiocarbonate moiety.[20] In addition, the terminal sulfur atom of the trithiocarbonate ligand is weakly interacting with the [K(18-crown-6)] cation as evidenced by the S-K bond distance of 3.172(4) Å. Two other nickel [CS_3]$^{2-}$ complexes are known, namely, [(dmpe)Ni(*S,S*:κ$_2$-CS_3)] (dmpe = $PMe_2CH_2CH_2PMe_2$) and [Et_4N]$_2$[(*S,S*:κ$_2$-CS_3)Ni(μ-SEt)$_2$Ni(*S,S*:κ$_2$-CS_3)], and each features comparable Ni-S and C-S metrical parameters.[16, 17]

The ^{1}H NMR spectrum of **1** in C_6D_6 is consistent with a C_{2v} symmetric, square planar Ni^{II} complex. For example, this spectrum features only one *tert*-butyl resonance, at 1.26 ppm. Likewise, the spectrum displays only two methyl resonances for the isopropyl substituents, which appear as doublets at 1.48 and 2.09 ppm. While our understanding of late metal sulfide reactivity is still relatively limited, early transition metal sulfides are widely known to react with CS_2 to yield trithiocarbonate complexes. For example, [V(η_2-S_2)(S)$_2$(SPh)]$^{2-}$ yields [V_2(μ_2-S_2)$_2$(*S,S*:κ$_2$-CS_3)$_4$]$^{4-}$, [MS_4]$^{2-}$ (M = Mo, Re) yields [M(*S,S*:κ$_2$-CS_3)$_4$]$^{3-}$, and [Mo_2S_6]$^{2-}$ yields [Mo_2(S)$_2$(μ-S)$_2$(*S,S*:κ$_2$-CS_3)$_2$]$^{2-}$, upon reaction with CS_2.[21-25]

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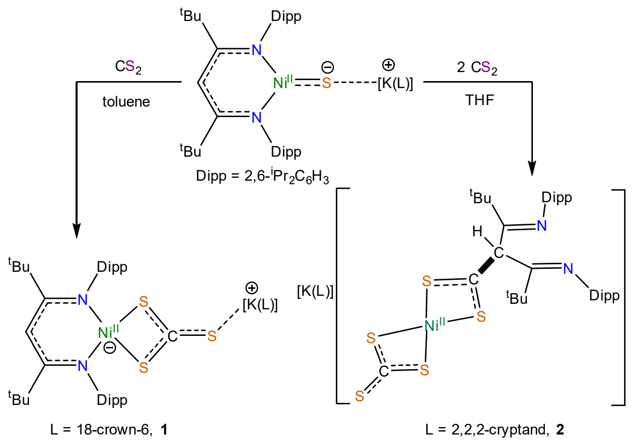

Scheme 1 Activation of CS_2 by $[K(L)][(L^{tBu})Ni^{II}(S)]$ to yield **1** and **2**.

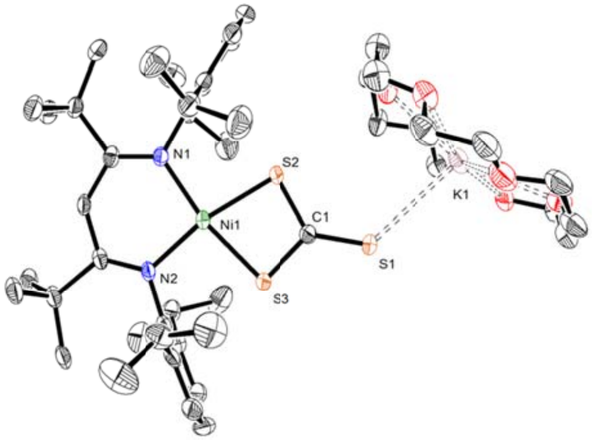

Figure 1 ORTEP drawing of $[K(18\text{-crown-6})][(L^{tBu})Ni^{II}(S,S{:}\kappa_2\text{-}CS_3)]$ ($\mathbf{1}\cdot C_7H_8$) shown with 50% thermal ellipsoids. Hydrogen atoms and C_7H_8 solvate have been omitted for clarity. Selected metrical parameters: Ni1-N1 1.929(3), Ni1-N2 1.940(3), Ni1-S2 2.235(1), Ni1-S3 2.210(1), S1-C1 1.666(4), S2-C1 1.697(4), S3-C1 1.696(4), S1-K1 3.172(4), N1-Ni1-N2 96.6(1)°, N1-Ni1-S2 94.93(9)°, N2-Ni1-S3 94.14(9)°, S2-Ni1-S3 74.29(4)°, S2-C1-S3 104.5(2)°, S2-C1-S1 129.5(2)°, S3-C1-S1 125.9(2)°.

Treatment of $[K(2,2,2\text{-cryptand})][(L^{tBu})Ni^{II}(S)]$ with 1 equiv of CS_2 in benzene immediately affords a bright red solution that slowly turns purple on standing. From this solution, $[K(2,2,2\text{-cryptand})][(S,S{:}\kappa_2\text{-}CS_3)Ni^{II}\{S,S{:}\kappa_2\text{-}CS_2(L^{tBu})\}]$ (**2**), the product of double CS_2 insertion, was isolated in 36% yield as a purple solid. Alternatively, complex **2** could be generated by reaction of $[K(2,2,2\text{-cryptand})][(L^{tBu})Ni^{II}(S)]$ with 2 equiv of CS_2 in THF (Scheme 1). Under these conditions, complex **2** was isolated in 55% yield. The formulation of complex **2** was confirmed through elemental analysis, VT ^1H NMR spectroscopy, and X-ray crystallography. Complex **2** features a square planar Ni center ((Σ(L-Ni-L) = 360°) coordinated by a $[CS_3]^{2-}$ ligand and a dithiocarboxylate $[CS_2(L^{tBu})]^-$ ligand (Figure 2). The $[CS_3]^{2-}$ ligand in **2** possesses C-S bond lengths of 1.66(1), 1.72(1), and 1.72(1) Å; similar to those observed in complex **1**. The $[CS_2(L^{tBu})]^-$ ligand contains nearly identical C-S bond lengths of 1.662(9) and 1.682(9) Å, while the newly formed C-C bond is 1.54(1) Å, consistent with a C-C single bond. The Ni-S bonds in **2** are within the range expected for Ni^{II}-S single bonds.[16-18] Also of note is the angle between the two N-C(β)-C(^{t}Bu) planes in the β-diketiminate fragment, which is 66(1)° and contrasts to complex **1,** where the angle is only 1.4(7)°. This angle results in an overall C_1 symmetric complex. The ^1H NMR spectrum of **2** at 25 °C (thf-d_8) is relatively featureless. Upon cooling to -75 °C the resonances sharpen considerably. This spectrum features two distinct *tert*-butyl resonances, at 1.27 and 1.13 ppm, consistent with the low symmetry of the solid state structure. Also present in the spectrum is a resonance at 5.50 ppm which we have assigned to the γ-CH environment (see figures S5 and S6). Examination of the solid state molecular structure of complex **2** suggests that slow rotation about C3-C4 and C3-C21 bonds would explain the broadening observed in the room temperature ^1H NMR spectrum.

In complex **2**, the $[CS_3]^{2-}$ moiety is the product of CS_2 activation by the sulfide ligand, while the dithiocarboxylate $[CS_2(L^{tBu})]^-$ ligand is the product of nucleophilic attack of a second equiv of CS_2 by the β-diketiminate γ-carbon. Nucleophilic bond forming reactions involving the β-diketiminate γ-carbon have been reported previously for O_2, NO, $OCCPh_2$, nitriles, and diazoacetate.[26-30] However, to our knowledge, this is the first example involving CS_2. Interestingly, reaction of $[K(18\text{-crown-6})][(L^{tBu})Ni^{II}(S)]$ with two equiv of CS_2 produces a product that we have tentatively identified as $[K(18\text{-crown-6})][(S,S{:}\kappa_2\text{-}CS_3)Ni\{S,S{:}\kappa_2\text{-}CS_2(L^{tBu})\}]$ (**3**) (i.e., the product of double CS_2 insertion) on the basis of the similarity of its ^1H NMR spectrum with that of complex **2** (See Figure S7).

To rationalize the difference in reactivity between the 18-crown-6 and 2,2,2-cryptand salts we suggest that the rate of CS_2 insertion into the putative intermediate, $[K(2,2,2\text{-cryptand})][(L^{tBu})Ni^{II}(S,S{:}\kappa_2\text{-}CS_3)]$, is faster than the rate of CS_2 insertion into complex **1**. We hypothesize that the faster rate of insertion exhibited by $[K(2,2,2\text{-cryptand})][(L^{tBu})Ni^{II}(S,S{:}\kappa_2\text{-}CS_3)]$ is due to the enhanced nucleophilicity of its β-diketiminate ligand, which results from the better separation of $[K(2,2,2\text{-cryptand})]^+$ cation from the anionic nickel fragment.

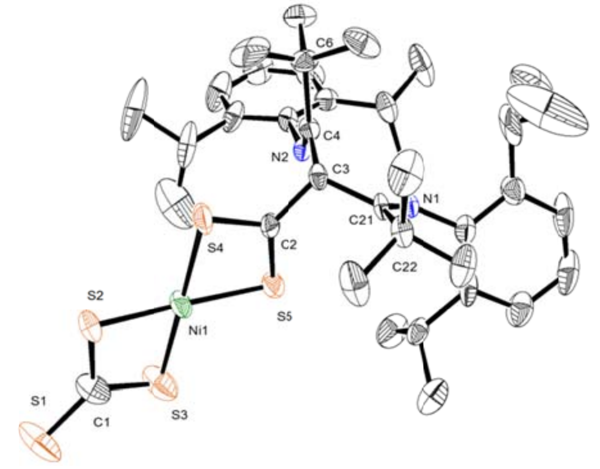

Figure 2 ORTEP drawing of [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS$_3$)Ni^{II}{*S,S*:κ$_2$-CS$_2$(L^{tBu})}] (**2**·C$_4$H$_{10}$O) shown with 50% thermal ellipsoids. Hydrogen atoms, [K(2,2,2-cryptand)]$^+$, and C$_4$H$_{10}$O solvate have been omitted for clarity. Selected metrical parameters: Ni1-S2 2.183(3), Ni1-S3 2.169(3), S1-C1 1.66(1), S2-C1 1.72(1), S3-C1 1.72(1), Ni1-S4 2.223(3), Ni1-S5 2.229(3), S4-C2 1.682(9), S5-C2 1.662(9), C2-C3 1.54(1), C3-C4 1.54(1), C3-C21 1.55(1), C4-N2 1.27(1), C21-N1 1.25(1), S1-C1-S2 126.0(7)°, S1-C1-S3 128.4(7)°, S2-C1-S3 105.6(6)°, S2-Ni1-S3 78.1(1)°, S2-Ni1-S4 101.5(1)°, S3-Ni1-S5 102.8(1)°, S4-Ni1-S5 77.7(1)°, S4-C2-S5 113.2(5)°.

In summary, the "masked" terminal nickel sulfide complex, [K(18-crown-6)][(L^{tBu})Ni^{II}(S)], readily activates CS$_2$ to give the trithiocarbonate product, [K(18-crown-6)][(L^{tBu})Ni^{II}(*S,S*:κ$_2$-CS$_3$)]. In contrast, [K(2,2,2-cryptand)][(L^{tBu})Ni^{II}(S)] preferentially reacts with CS$_2$ to generate the double insertion product, [K(2,2,2-cryptand)][(*S,S*:κ$_2$-CS$_3$)Ni^{II}{*S,S*:κ$_2$-CS$_2$(L^{tBu})}]. We attribute this difference in reactivity to the difference in the rate of the second CS$_2$ insertion reaction between the two systems. This work also confirms the nucleophilicity of the sulfide ligand in [(L^{tBu})Ni^{II}(S)]$^-$ and further expands the scope of reactivity for late metal terminal sulfide complexes. Future work will continue to focus on the fundamental chemistry of nickel sulfides, including the activation of other small molecules.

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