Nickel Chalcogenides

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# Facile Dissociation of $[(LNi^{II})_2E_2]$ Dichalcogenides: Evidence for $[LNi^{II}E_2]$ Superselenides and Supertellurides in Solution**

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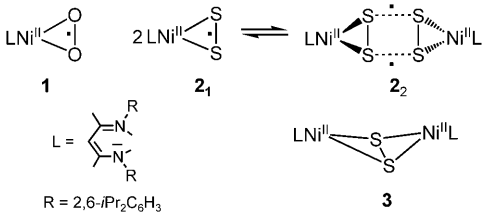
*Dedicated to Professor Yitzhak Apeloig on the occasion of his 65th birthday*

Transition-metal complexes containing diatomic chalcogen ligands $E_2$ have attracted increasing interest because of their intriguing structures,[1] synthetic applications,[2] catalytic reactivity,[3] and biological significance.[4] Among such dichalcogen derivatives, the chemistry of the Group 10 (nickel group) metal complexes deserves particular attention. In fact, a number of $d^8$-nickel-group-metal dichalcogenide complexes with redox properties have been synthesized and structurally characterized. Strikingly and in contrast to the substantial knowledge on peroxo and persulfido $d^8$-metal systems,[1–6] the corresponding chemistry of the heavier dichalcogen ligands $Se_2$ and $Te_2$ is mostly unexplored as yet, probably because of their reduced stability and high propensity to undergo concatenation in comparison to that of the $O_2$ and $S_2$ entities.[7–9] Up to now, only a few mononuclear side-on $ME_2$ (M = Group 10 metal, E = Se, Te) and doubly bridged dinuclear $M_2E_2$ butterfly-like complexes have been reported; however, their bonding situation and reactivity pattern are hardly investigated.[1c,7–9]

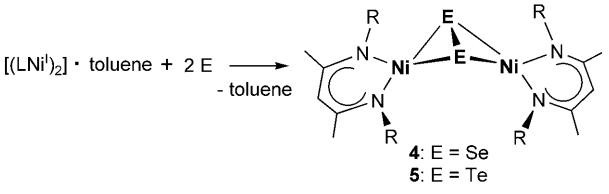
Recently we have successfully synthesized the first isolable superoxide $[LNiO_2]$ (**1**; L = β-diketiminiate, CH(CMeNR)$_2$, R = 2,6-*i*Pr$_2$C$_6$H$_3$)[10] and its supersulfide analogue $[LNiS_2]$ (**2$_1$**; Scheme 1),[11] by activation of $O_2$ and $S_8$ using the dimeric β-diketiminate nickel(I) precursor $[(LNi^I)_2]\cdot C_6H_5CH_3$.[12] Moreover, mixtures of **2$_1$** and it dimer **2$_2$** (Scheme 1) react with the precursor $[(LNi^I)_2]\cdot C_6H_5CH_3$ at room temperature to yield solely the diamagnetic dinuclear nickel(II) disulfide complex $[(LNi^{II})_2S_2]$ (**3**; Scheme 1). Herein, we report the facile formation of the selenium and tellurium analogues of **3**, that is, $[(LNi^{II})_2Se_2]$ (**4**) and $[(LNi^{II})_2Te_2]$ (**5**), which, surprisingly, undergo facile dissociation in toluene solutions to give the first experimental evidence for the formation of the Se and Te analogues of the superchalcogenide pair **2$_1$**/**2$_2$**.




***Scheme 1.*** Dichalcogen nickel(II) complexes **1**–**3** supported by the β-diketiminate ligand L.

As previously described,[10,11] the nickel superoxide **1** and its supersulfide **2$_2$** are readily accessible by low-temperature activation of $O_2$ and $S_8$, respectively, starting from $[(LNi)_2]\cdot C_6H_5CH_3$. In contrast, elemental selenium and tellurium react very slowly even at ambient temperature, leading merely to the selenium and tellurium analogous of **3**, that is, compound **4** and **5** (Scheme 2). These were isolated in the form of brown crystals in 84% (**4**) and 89% yield (**5**). The new compounds are sensitive to air and moisture and marginally soluble in hexane, but dissolve well in arenes and ethereal solvents.

The compositions of **4** and **5** were confirmed by correct elemental analysis (C, H, N; see Supporting Information). Their molecular structures were determined by X-ray diffraction analyses (Figure 1). The isomorphous compounds




***Scheme 2.*** Synthesis of **4** and **5** from $[(LNi)_2]\cdot C_6H_5CH_3$; L = β-diketiminate (R = 2,6-*i*Pr$_2$C$_6$H$_3$).

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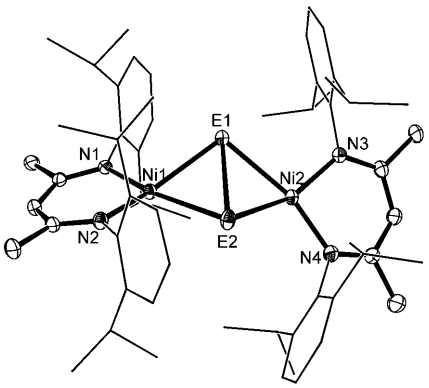


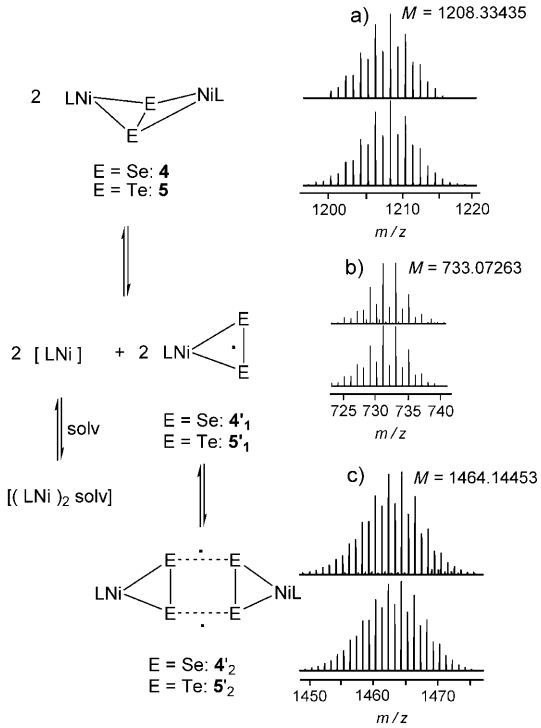

***Figure 1.*** Molecular structure of **4** (E = Se) and **5** (E = Te). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: Se1–Se2 2.3304(6), Se1–Ni1 2.3375(6), Se1–Ni2 2.3430(6), Ni1–Se2 2.3294(6), Se2–Ni2 2.3019(6); N1-Ni1-N2 95.6(2), N4-Ni2-N3 96.3(1); Selected bond lengths [Å] and angles [°] for **5**: Te1–Te2 2.6994(3), Te1–Ni1 2.5123(4), Te1–Ni2 2.5419(4), Te2–Ni2 2.4937(4), Te2–Ni1 2.5426(4); N1-Ni1-N2 95.7(1), N4-Ni2-N3 96.2(1).

adopt the expected butterfly-like structure with a $\{Ni^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}E_2)\}$ (E = Se, Te) core, similar to the structure of **3**.[11]

Compound **4** is the first structurally characterized complex with a $\{Ni^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Se_2)\}$ core. The Ni–Se distances in **4**, ranging from 2.3019(6) to 2.3430(6) Å, are only slightly longer than those observed in $[(Se_2WSe_2)Ni(Se_2)]^{2-}$ (2.299 Å),[8a] which bears a terminal dianionic side-on coordinate $Se_2$ ligand. The Se–Se distance of 2.3304(6) Å in **4** is similar to those observed for related terminal $\eta^2$-$Se_2$ complexes.[8] The Ni–Te distances in **5**, ranging from 2.4937(4) to 2.5426(4) Å, are shorter than those found in $[(MeC\{CH_2PPh_2\}_3)_2Ni_2Te_2]$ (2.587 Å),[9a] containing five-coordinate $d^8$ Ni centers in the $\{Ni^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}Te_2)\}$ core. The Te–Te distance of 2.6994(3) Å in **5** is close to the value observed in $[\{(Et_3P)_2Pt\}_2Te_2]$ (2.695(1) Å)).[9b] Remarkably, the Te–Te distance in **5** is much shorter than that in the nickel complex $[(MeC\{CH_2PPh_2\}_3Ni)_2Te_2]$ (2.802(1) Å).[9a]

As expected, **4** and **5** are diamagnetic (closed-shell) complexes in the solid state. However, to our surprise, dissolution of crystals in toluene leads to clear, red-brown solutions containing open-shell species as indicated by sharp, paramagnetically shifted resonance signals in the $^1$H NMR spectra at room temperature (see Supporting Information). This behavior is in marked contrast to that of **3** which remains diamagnetic in toluene solutions even at 80 °C.[11] The most unusual paramagnetic shifts for the resonances of **4** and **5**, respectively, are observed for the γ-ring proton on the $C_3N_2Ni$ rings and the terminal methyl protons, which give rise to singlets at $\delta = -8.62$ and $-2.37$ ppm for **4** and $\delta = -21.06$ and $-6.32$ ppm for **5**, respectively. Variable temperature experiments of **5** in [$D_8$]toluene revealed that the resonance signals undergo a drastic downfield shift at lower temperature.

Applying the Evans-method[13] for the determination of the magnetic moment to **4** and **5** dissolved in [$D_6$]benzene gave merely 1.06 and 1.86 $\mu_B$ at room temperature. These low magnetic values already suggest the presence of paramagnetic species in equilibrium with diamagnetic ones. Therefore we propose that the facile dissociation process leads to the paramagnetic superchalcogenide[14] [$LNiSe_2$] (**4′$_1$**) or [$LNiTe_2$] (**5′$_1$**), and liberation of the nickel(I) precursor [$LNi^I$] in equilibrium with the starting material (**4** or **5**) as well as with their corresponding diamagnetic dimers (**4′$_2$**, **5′$_2$**, and $[(LNi^I)_2]\cdot C_6H_5CH_3$; Scheme 3). In fact, the presence of the

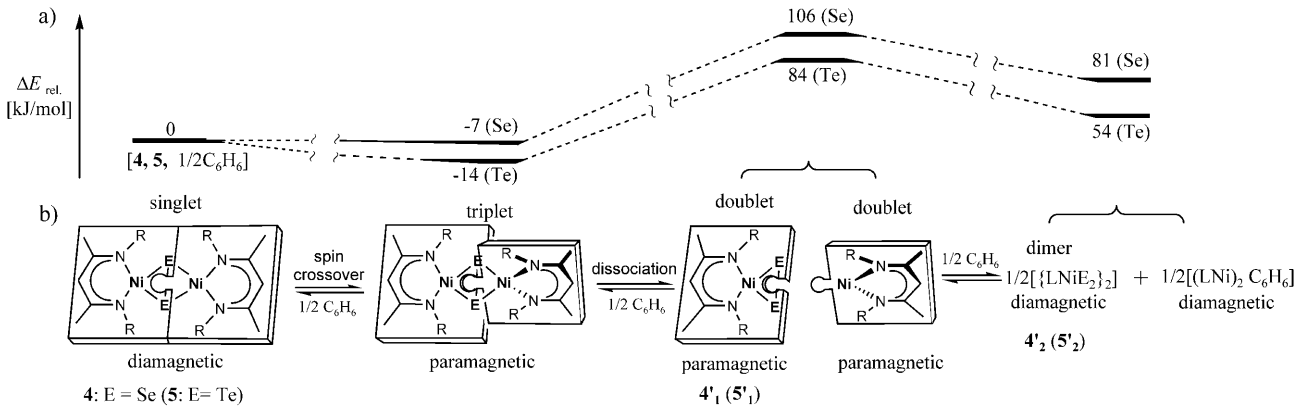



***Scheme 3.*** left: Proposed dissociation of **4** and **5** in solution; right: Detection of the molecular ions of **5** (a), **5′$_1$** (b), and **5′$_2$** (c) in THF solutions by high-resolution ESI-MS (in each case, top: experimental, bottom: simulated).

dissociation products **4′$_1$**/**4′$_2$** and **5′$_1$**/**5′$_2$** in solutions of **4** and **5**, respectively, is well supported by high-resolution electrospray ionization mass spectrometry (HR ESI-MS) (Scheme 3, right; see Supporting Information for details). Notably, the HR ESI-MS spectrum of **3** precludes the presence of the corresponding fragments **2$_1$** or **2$_2$**, consistent with the diamagnetic nature of **3** in solution.[15] Density functional theory (DFT) calculations (see Supporting Information) support the facile formation of the superchalcogenides **4′$_1$** and **5′$_1$** under concomitant reductive elimination of [$LNi^I$] from **4** and **5**, respectively (Scheme 4). The calculated reaction energies for the dissociation of **4** and **5** into **4′$_1$** and **5′$_1$** are 106 and 84 kJ mol$^{-1}$, respectively, revealing that the dissociation of **5** occurs more easily than that of **4**. Additionally, the dissociation process involves a spin crossover from singlet to triplet state (Scheme 4).

Notably, the triplet states of **4** and **5** are found to be more stable than the singlet state. In the triplet structures, one of the $d^8$ Ni centers achieves a tetrahedral coordination with high-spin configuration ($S = 1$), while the other one remains square-planar coordinated with low-spin configuration ($S = 0$). This situation is reminiscent of that observed for a related




***Scheme 4.*** a) Simplified DFT-derived energy profile; b) A representation of the dissociation of **4** and **5** in the presence of benzene to give $\mathbf{4'_1}$, $\mathbf{5'_1}$, [LNi], and the dimers $\mathbf{4'_2}$, $\mathbf{5'_2}$, and $[(LNi^{I})_2]$ $C_6H_6$, respectively.

$\mu_2$-bis(hydroxo) $\{Ni^{II}_2(OH)_2\}$ complex.[10] For energetic reasons, it seems likely that the dissociation of **4** and **5** occurs via their triplet states. Additionally, dimerization of $\mathbf{4'_1}$, $\mathbf{5'_1}$, and [LNi] in the presence of benzene facilitates the dissociation process significantly by at most 30 kJ mol$^{-1}$ (Scheme 4). Although the barrier for spin crossover of **4** and **5** from the respective singlet to the triplet state could not be calculated, it is clear that the rotational barrier is lower when the distance between the two LNi moieties is increased. In other words, the increasing Ni···Ni distance in the series 3.591 Å (**3**), 3.715 Å (**4**), and 3.968 Å (**5**) intuitively explains that dissociation for **5** is easier than for **4**. As expected, the unpaired electron in $\mathbf{4'_1}$ and $\mathbf{5'_1}$ is almost completely located in a $\pi^*$ orbital of the $E_2$ superchalcogenide ligand (Figure 2), similar to the situation observed in **1**.[10]

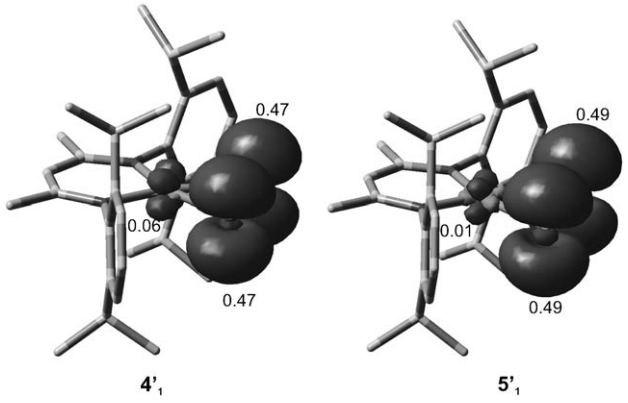
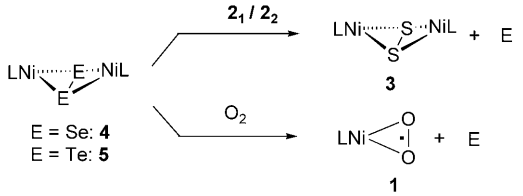



***Figure 2.*** Calculated spin density of $\mathbf{4'_1}$ and $\mathbf{5'_1}$.

Interestingly, treatment of **4** and **5** with $\mathbf{2_1}/\mathbf{2_2}$ in the molar ratio of 1:2 at ambient temperature leads to the formation of **3** along with elemental selenium and tellurium, respectively (Scheme 5). Apparently, the conversion of $\mathbf{2_1}/\mathbf{2_2}$ with **5** occurs much faster than that with **4**, as shown by NMR spectroscopy. Although the mechanism is still unknown and intermediates could not be detected, it seems likely that $\mathbf{4'_1}$ and $\mathbf{5'_1}$, respectively, act as transient species in this remarkable chalcogen exchange reactions.




***Scheme 5.*** Conversion of **4** and **5** with $\mathbf{2_1}/\mathbf{2_2}$ and $O_2$ to give **3** and **1**, respectively.

Moreover, both **4** and **5** react readily with dry dioxygen at room temperature, leading to the formation of **1** as main product ($^1$H NMR, EPR spectroscopy). Surprisingly, an intermediate with the composition $[\mathbf{5} + O_2]$ could be detected by ESI-MS experiments [$m/z = 1240.32495$ (calcd 1240.32461)], but could not be isolated to date owing to fast liberation of elemental tellurium.

In summary, we have synthesized the β-diketiminate-ligand-supported $Ni_2E_2$ butterfly complexes **4** and **5** featuring a $\{Ni^{II}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}E_2)\}$ (E = Se, Te) core. Although **4** and **5** are diamagnetic in the solid state, they undergo facile dissociation in solution to give the respective paramagnetic superselenide and supertelluride complexes $\mathbf{4'_1}$ and $\mathbf{5'_1}$ along with [LNi]; these species are in equilibrium with their corresponding diamagnetic dimers $\mathbf{4'_2}$, $\mathbf{5'_2}$, and $[(LNi)_2]$·solv, respectively. Evidence for the formation of the unique types of superchalcogenide species from **4** and **5** is provided from HR-ESI mass spectrometry, DFT calculations, and additionally underlined by the unusual reactivity of **4** and **5** towards $\mathbf{2_1}/\mathbf{2_2}$ and $O_2$, respectively.

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[15] The protonated ion of **3** detected by HR ESI-MS: *m*/*z*: calculated for $[\mathbf{3}+H]^+$ ($C_{58}H_{83}N_4Ni_2S_2$): 1015.4777, found: 1015.4760. The fragment ion $[LNiS_2]$ $\mathbf{2_1}$ or its dimer $[\{LNiS_2\}_2]$ ($\mathbf{2_2}$) could not be detected.

  