Lithium Alkylselenolates and -tellurolates – A Solid-State and Solution Structural Study

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Facile insertion of elemental Se or Te into the C–Li bond of *n*BuLi in the presence of TMEDA gives [*n*BuXLi·TMEDA]$_2$ (X = Se **1**; Te **2**). Both **1** and **2** have been fully characterised in the solid and solution states resulting in the first crystal structures of a lithium alkylselenolate and -tellurolate and giving a unique insight into the coordination chemistry of the less sterically demanding chalcogenolate ligands.

Introduction

The desire for new and efficient syntheses for both metal chalcogenolates (primarily used as precursors to semiconducting metal chalcogenolides[1] and as model systems for various biologically active metalloproteins[2]) and also for new reagents for the synthesis of selenium- and tellurium-containing organics[3] has resulted in a growing interest in alkali metal complexes with selenolate (RSe^-) and tellurolate (RTe^-) ligands. However, there still remains a scarcity of both solid-state and solution studies of these species, especially when compared to the multitude of data available on the analogous alkali metal alkoxide (RO^-) and thiolate (RS^-) complexes.[4] Moreover, the majority of studies to date have utilised sterically bulky ligands, such as substituted silyl chalcogenolates (R_3SiX^-; R = Me, SiMe$_3$; X = Se, Te)[5–9] or substituted aromatics (Mes*X$^-$; Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$; X = Se, Te)[10–12] so as to confer extra kinetic stability upon the resulting complex. To the best of our knowledge the only other examples of alkali-metal organochalcogenolates to be structurally characterised are the 2,2′-bipyridine complexes [PhSeLi·bipy]$_2$ and [2-PyrSeLi·bipy]$_2$,[13] the phenylacetyl selenolate PhC≡CSeLi·TMEDA·THF[14] and the heterobimetallic species [CpFe{C$_5$H$_3$(CH$_2$NMe$_2$)TeLi·DME}],[15] [(C$_5$H$_5$)$_2$Lu(μ-SePh)$_2$Li·2THF][16] and [(py)$_2$Yb(SePh)$_2$(μ-SePh)$_2$Li(py)$_2$] (py = pyridine).[17] In order to confront this lack of structural knowledge, particularly of the less sterically demanding ligands, we report here the first solid-state characterisation of both a lithium alkylselenolate (*n*BuSeLi·TMEDA)$_2$ (**1**) and -tellurolate (*n*BuTeLi·TMEDA)$_2$ **(2)** [TMEDA = (Me$_2$NCH$_2$)$_2$].

Results and Discussion

Two main synthetic routes have been documented for the preparation of lithium chalcogenolates: metallation of an organic acid (RSeH or RTeH) and insertion of elemental Se or Te into a C–Li or Si–Li bond.[2,3] The second of these procedures was employed in the synthesis of **1** and **2** since it provided a clean, high yield of the desired products and avoided the synthesis of the readily oxidised butylselenol and butyltellurol species. Reaction in toluene of *n*BuLi with elemental Se or Te (1:1 ratio) in the presence of TMEDA (1 equivalent) resulted in the dissolution of the Group 16 element to give a clear pale yellow solution from which it proved possible to grow, at room temperature, crystals of the lithium chalcogenolates **1** and **2** in yields 36 and 52%, respectively. Both **1** and **2** are highly air sensitive and extremely pungent compounds.

A low temperature X-ray structural characterisation of **1** and **2** reveals that they both crystallise in the monoclinic space group *I*2/*a* and that they both contain two isostructural dimeric molecules within the asymmetric unit, each of which exhibits twofold symmetry (Figure 1). These dimeric units are based around a central Li$_2$X$_2$ (X = Se, Te) ring with the *n*-butyl groups in a *cis* conformation and each of the lithium ions solvated by one TMEDA molecule. The free ends of the butyl groups are disordered in the solid-state structures of both **1** and **2**. The Se–Li mean average bond length in **1** [2.583 Å; range 2.544(17) to 2.592(15) Å] is comparable to the Se–Li bond lengths of previously studied lithium selenolates [range 2.462(13) to 2.622(8) Å].[5,11–14] However, the Se–C bond lengths in **1** [1.98(1) and 2.02(2) Å] are longer than the Se–C bonds in the previously characterised arylselenolates [range 1.896(4) to 1.942(7) Å][11–13] and also longer than the Se-C bond [1.813(4) Å] in the alkylnylselenolate [PhC≡CSe-Li·TMEDA·THF].[14] This can be accounted for by the sp^3 hybridisation of the α-carbon in **1** whose larger, more diffuse orbitals form longer bonds than the α-carbon sp^2 hybrid orbitals in the arylselenolates and the α-carbon sp orbitals in the alkynylselenolate. The C–Se–Li angle [mean 95.8°, range 92.9(5) to 97.4(7)°] is more acute than in any

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other selenolate previously reported [range 98.2(3) to 104.3(2)°][11−14] presumably by virtue of the low steric demands of the *n*-butyl group. The Li−Se−Li inter-ring angle is also very acute, 69.2(6) and 70.1(6)° in **1** *cf.* 77.0(2) and 75.8(4)° in the only other dimeric lithium selenolates [Li(DME)SeSi(SiMe$_3$)$_3$]$_2$ [5] and [Li(bipy)(SePh)]$_2$,[13] respectively.

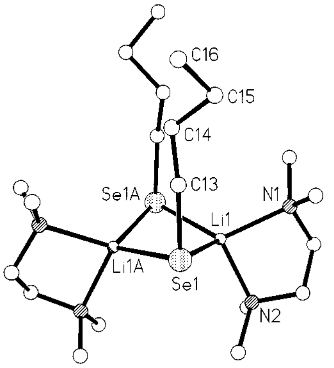

Figure 1. The solid-state structure of [*n*BuSeLi·TMEDA]$_2$ (**1**); only one of the two isostructural dimers in the asymmetric unit is shown; hydrogen atoms and disorder in the *n*-butyl group are omitted for clarity; the molecule lies on a crystallographic twofold rotation axis which relates Li1 and Se1 to Li1A and Se2A

In **2** the Te−Li distances [mean 2.813 Å, range 2.802(6) to 2.824(6) Å] are similar to previously reported Li−Te distances [range 2.70(1) to 2.88(2) Å][6−10,15] and the Te−C (sp^3) distances of 2.259(11) and 2.191(4) Å are larger than the Te−C(sp^2) distances of 2.142(2) Å in [(*o*-C$_6$H$_4$CH$_2$NMe$_2$)TeLi(DME)], 2.184(4) Å in [Mes*TeLi(THF)$_3$][10] and 2.122(2) Å in [CpFe{C$_5$H$_3$(CH$_2$NMe$_2$)TeLi·DME}].[15] The Li−Te−Li bond angles [both of which are 68.2(2) °] are more acute than those observed [75.1(1) °] in the only other dimeric lithium tellurolate [(DME)LiTeSi(SiMe$_3$)$_3$]$_2$,[9] and the mean C−Te−Li bond angle in **2** is 95.0° [range 93.5(2) to 97.2(2)°].

In addition to solid-state X-ray diffraction studies, the solution structures of both **1** and **2** were probed by multinuclear NMR spectroscopy and crysocopic relative molecular mass measurements. Cryoscopic measurements on a 0.030 M solution of **1** in benzene indicated an average association value *n* for [BuSeLi·TMEDA]$_n$ of 3.17 ± 0.08. One possible explanation of this association value is that in nondonor solvents a dimer/tetramer equilibrium is occurring, in which the tetramer is formed from the back-to-back stacking of two of the *cis* dimeric units to give a Li$_4$Se$_4$ cubane structure. A similar result was obtained with a 0.030 M solution of **2** ($n = 3.30 \pm 0.12$). Despite this, ^{7}Li NMR spectroscopic studies at 25 °C on THF solutions of **1** and **2** showed only one peak ($\delta = -0.04$ for a 0.023 M solution of **1**, and $\delta = 0.25$ for a 0.020 M solution of **2**, referenced to PhLi in THF) indicating that any fluxional behaviour between different aggregation states is rapid. This dynamic equilibrium was still observed down to temperatures as low as −80 °C since even at these temperatures only one peak was visible by ^{7}Li NMR spectroscopy. The absence of any observable ^{7}Li coupling to either ^{77}Se or ^{125}Te in these spectra is also indicative of the fluxional behaviour of these species, since any change in aggregation state would involve the breaking and formation of Li−X (X = Se or Te) bonds. As expected, the ^{1}H and ^{13}C NMR spectra of **1** and **2** in [D$_6$]DMSO showed peaks attributable to the TMEDA and *n*-butyl groups, while the main difference between the two ^{13}C NMR spectra was the position of the α-carbon atoms: $\delta = -1.1$ in **1** and $\delta = -19.4$ in **2**. In addition, $^1J_{CTe}$ coupling was observed in the ^{13}C spectrum of **2**, with a coupling constant of 158.0 Hz (this is comparable to previously reported values for dialkyl tellurides).[18] It proved impossible to see Se−C coupling in the ^{13}C NMR spectrum of **1** due to the ready decomposition of this product, hence the poor resolution of its spectra. However, ^{77}Se{^{1}H} NMR spectroscopy of **1** was undertaken and showed a single peak at $\delta = -660$ (referenced to SeMe$_2$ at $\delta = 0$); again no Se−Li coupling was observable.

We now hope to extend this work to look at other sterically undemanding lithium chalcogenolates and also their transmetallation reactions, with particular emphasis placed upon their possible utility in the synthesis of single source precursors to semiconducting materials.[1]

Experimental Section

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen using standard double manifold and glove-box techniques.

[*n*BuSeLi·TMEDA]$_2$ (1): *n*BuLi (3.2 mL, 1.6 M in hexanes, 5.0 mmol) was added to a suspension of Se (0.40 g, 5 mmol) in toluene (10 mL) and TMEDA (0.75 mL, 5 mmol) under nitrogen at −78 °C. The mixture was then allowed to warm to room temperature with constant stirring to give a pale yellow solution. This solution was filtered under nitrogen and reduced in volume under vacuum to approximately 3 mL. Hexane (6 mL) was then added and the solution left at room temperature for 24 hours to yield a batch of yellow crystalline needles (0.46 g, 36%). − M.p. 128−130 °C. − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.64 (t, 2 H, -C*H*$_2$Se-), 2.23 (s, 12 H, TMEDA), 2.13 (s, 4 H, TMEDA), 1.95 (m, 2 H, -C*H*$_2$-), 1.64 (m, 2 H, -C*H*$_2$-), 1.11 (t, 3 H, C*H*$_3$CH$_2$-).

[*n*BuTeLi·TMEDA]$_2$ (2): *n*BuLi (3.2 mL, 1.6 M in hexanes, 5.0 mmol) was added to a suspension of Te (0.644 g, 5 mmol) in toluene (15 mL) and TMEDA (0.75 mL, 5 mmol) under nitrogen at −78 °C. The mixture was then allowed to warm to room temperature with constant stirring to give an orange solution. This solution was filtered under nitrogen and left at room temperature for two days to yield a batch of dark-orange, needle-shaped crystals (0.80 g, 52%). − M.p. 144−148 °C. − ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 2.59 (t, 2 H, -C*H*$_2$Te-), 2.25 (s, 12 H, TMEDA), 2.05 (s, 4 H, TMEDA), 1.92 (m, 2 H, -C*H*$_2$-), 1.59 (m, 2 H, -C*H*$_2$-), 1.03 (t, 3 H, C*H*$_3$CH$_2$-).

X-ray Analysis: Crystals of **1** and **2** were mounted directly into the cold stream of an Oxford Crysotream crystal cooling apparatus, installed on either a Stoe−Siemens four-circle diffractometer (**1**) or a Siemens SMART CCD diffractometer (**2**), using perfluoropolyether oil.

Crystal data for 1: C$_{20}$H$_{50}$Li$_2$N$_4$Se$_2$, $M = 518.44$, monoclinic, space group $I2/a$, $a = 16.736(4)$, $b = 19.744(5)$, $c = 17.730(4)$ Å, $\beta =$

91.13(3)°, $U = 5857(2)$ Å^3, $Z = 8$, $D_c = 1.176$ g cm^{-3}, μ(Mo-K_α) = 2.535 mm^{-1}, $T = 180(2)$ K. 5916 Reflections (5145 unique, $R_{\text{int}} = 0.064$) measured. Refinement on F^2 values of all data gave final $wR2 = 0.2195$, conventional $R = 0.0795$ on F values of all reflections with $F^2 > 2\sigma(F^2)$, 292 parameters.

Crystal data for 2: $C_{20}H_{50}Li_2N_4Te_2$, $M = 615.72$, monoclinic, space group $I2/a$, $a = 17.762(1)$, $b = 19.811(2)$, $c = 17.339(1)$ Å, β = 90.77(1) °, $U = 6101.0(8)$ Å^3, $Z = 8$, $D_c = 1.341$ g cm^{-3}, μ(Mo-K_α) = 1.923 mm^{-1}, $T = 160(2)$ K. 27244 Reflections (7512 unique, $R_{\text{int}} = 0.036$) measured. Refinement on F^2 values of all data gave final $wR2 = 0.1082$, conventional $R = 0.0375$ on F values of all reflections with $F^2 > 2\sigma(F^2)$, 291 parameters.

Crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-151235 (**1**) and CCDC-152141 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [Fax (internat.): +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk].

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