# Lithium 2,2,6,6-Tetramethylpiperidinoselenolate: An Unsymmetrical Dimer with an Unusually Coordinated Lithium

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Lithium 2,2,6,6-tetramethylpiperidide inserts elemental selenium into its Li−N bond with the formation of lithium 2,2,6,6-tetramethylpiperidinoselenolate **1**. In the crystal **1** is an unsymmetric dimer. One lithium atom is coordinated tetrahedrally by two molecules of tetrahydrofuran and two selenium atoms, the other lithium atom exhibits an approximately rectangular-planar coordination by two N,Se-chelating groups. The lithium atoms are bridged by two selenium atoms thus forming a planar $Li_2Se_2$ core. Ab initio Hartree-Fock calculations show **1** and the hypothetical symmetric dimer **2** to be of equal energy, whereas the non-chelated dimer **3** is of distinctly higher energy. Exclusive crystallization of **1** is most likely a consequence of its large dipole moment of 6.18 D. Calculations also show that the deformation of the observed geometry around the uniquely coordinated lithium atom in **1** towards distorted tetrahedral or complete planarity leads to an increase of energy. Excessive charge transfer from selenium to nitrogen explains the overwhelming tendency for the N,Se-chelating bonding

Organolithium compounds or, in an even broader sense, organoelementlithium compounds are attracting attention, partly because they are widely used in organic and organometallic syntheses and partly because of their often intriguing structures[1]. Only a few structures of lithium complexes of group 16 elements, especially of selenium and tellurium have been reported so far[2], although thiolates, selenolates, and tellurolates containing sterically very demanding organic residues proved to be valuable for the preparation of metal complexes with low coordination numbers[3]. Such compounds are of potential importance as single-source precursors for the preparation of semiconducting metalchalcogene phases by CVD processes[4]. Surprisingly, the first accurate lithium−selenium bond length was determined as late as 1991 by du Mont[2c] and confirmed a short time later for lithium supermesityl-selenolate[2d]. Despite the wealth of information about organonitrogen-lithium compounds[5], no structure has previously been reported for a lithium aminochalcogenolate.

## Results and Discussion

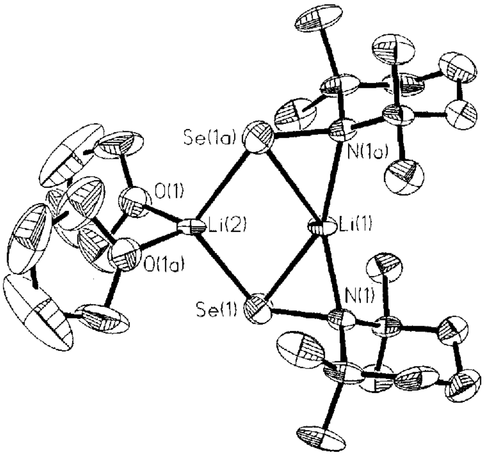
We found that a number of lithium salts of amines insert elemental selenium just like carbanions[6] with the formation of aminoselenolates[7] (eq. 1).

(1)

1

We used such anions in situ as starting materials for the preparation of diaminodi-, tri-, and tetraselanes[7]. In general aminoselenolates are unstable above about −10 °C against disproportion and also decompose in contact with moisture or oxygen. Since **1** appears to be one of the more stable aminoselenolates, we isolated and crystallized it. The molecular structure of **1** was determined by single-crystal X-ray diffraction (Figure 1). Selected bond length and angles are given.

Figure 1. Crystal structure of **1**, probability of thermal ellipsoids 50%, hydrogen atoms omitted[a]



[a] Selected bond lengths [pm] and bond angles [°] of **1**: Li(1)−Se(1) 253.2(7), Li(1)−N(1) 204.6(6), Li(2)−Se(1) 256.3(8), Se−N(1) 196.3(4), O(1)−Li(2) 198.9(10); O(1)−Li(2)−O(1a) 98.6(7), O(1a)-−Li(2)−Se(1) 119.9(2), Li(1)−Se(1)−Li(2) 65.6(3), Se(1)−Li(2)−Se(1a) 113.3(5), Se(1)−Li(1)−Se(1a) 115.5(5), N(1)−Li(1)−N(1a) 156.3(8), N(1a)−Li(1)−Se(1a) 49.4(2), N(1)−Se(1)−Li(1) 52.3(3), N(1)−Li(1)−Se(1) 49.4(2).

A dimeric aggregate with crystallographic $C_2$-symmetry was found which exhibits a number of noteworthy features. It is an unsymmetric dimer with one lithium atom, Li(2) coordinated tetrahedrally by two THF molecules and two selenium atoms of the planar $Li_2Se_2$ core. The other lithium

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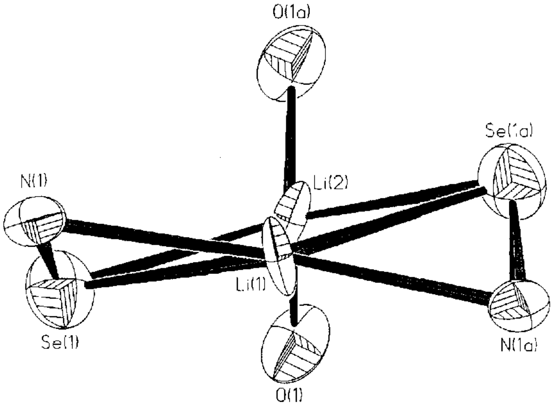
atom, Li(1) is tetracoordinated by two selenium atoms and two nitrogen atoms in an unique fashion. The coordination geometry is best described as nearly rectangular planar. Nitrogen atoms are only 43.3(2) pm, selenium atoms only 40.3(2) pm out of the best Se(1)−N(1)−Se(1a)−N(1a) plane, which mandatory contains Li(1) due to the molecular $C_2$-symmetry (Figure 2). Square-planar lithium centers are rare but have been observed in very rigid ligand systems such as lithium porphyrins[8], phthalocyanine[9], and in Li(acac)$_2^-$ anions[10].

Figure 2. Coordination geometry of Li(1) and Li(2) as seen approximately along $C_2$



If the formation of **1** as a dimer is taken for granted, intuitively one would predict it to be symmetrical like structures **2** (Figure 3) or **3** (Figure 4), which both would relieve the steric strain on the uniquely coordinated Li(1) and a structure related to **3** has been observed for [(THF)LiTeSi(SiMe$_3$)$_3$]$_2$[11].

Figure 3. Hypothetical structure of **2**

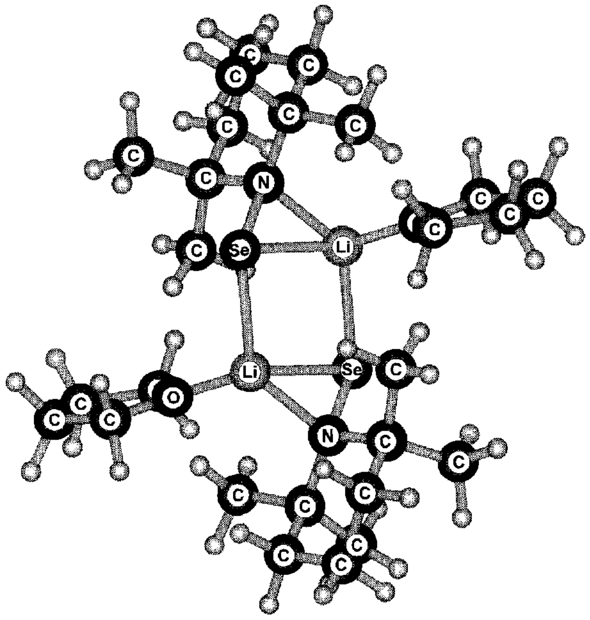
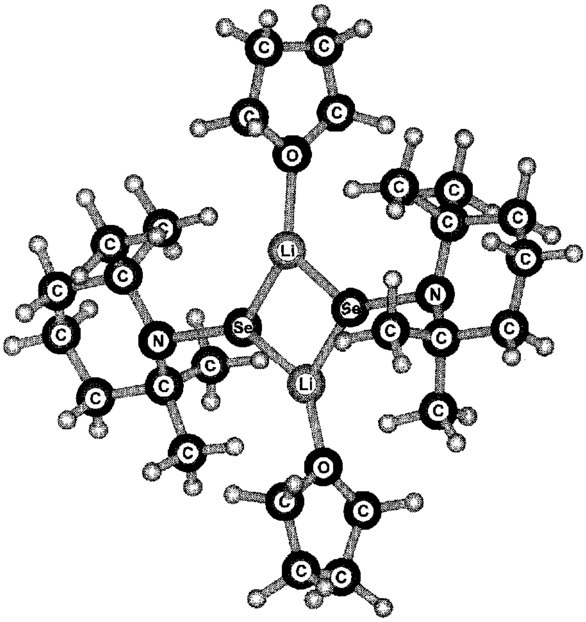


Figure 4. Hypothetical structure of **3**



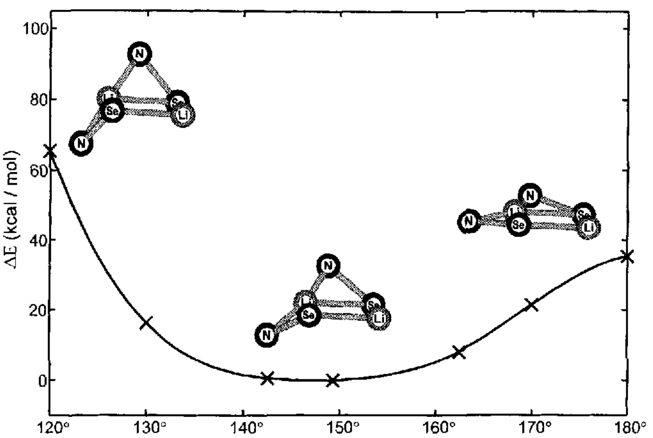
To possibly gain a better understanding for the prevalence of **1**, we performed ab initio Hartree-Fock calculations using the LANL2DZ[12] effective core potentials and basis sets as implemented in the Gaussian 94[13] set of programs for **1**, **2** and **3**. Attaching the hydrogen atoms at standard positions leads to 400 basis functions. Complete geometry optimization gave relative energies of 0, +5, and +125 kcal/mol for **1**, **2**, and **3**, respectively. This supports chemical intuition to some extent since **1** and **2** are indeed of equal energy within the error limits, whereas **3** is of distinctly higher energy. Remarkably, for **1** the interplanar angle between the Li(1)−Se(1)−Li(2)−Se(1a) plane and the Li(1)−Se−N plane is calculated as 148° at the energy minimum and thus almost coincides with the 149.3° from the X-ray structure. While such an excellent agreement is probably fortuitous, it nevertheless shows that packing effects do not dominate the molecular structure.

In addition, to get a specific look at the coordination geometry of Li(1), we changed the above interplanar angles, by rotating the two Li(1)−Se−N triangles, together with the structural residues attached to the nitrogen atoms around the Li(1)−Se axis while maintaining the $C_2$-symmetry of the molecule. The corresponding potential energy curve (Figure 5) is shallow and shows a smooth uprise to complete planarity around Li(1), whereas there is a steep ascent in the direction of a coordination geometry of Li(1) which is best described as irregular tetrahedral.

Purely qualitative VSEPR-considerations would predict exact planar coordination around Li(1) and the highest repulsion at 90°. The sum of the angles of the two closest variable contacts [N(1)−Li(1)−N(2) and N(1)−Li(1)−Se(2)] are 245.6° at 90°, 306.8° at 149.3° and 310.6° at 180°, respectively.

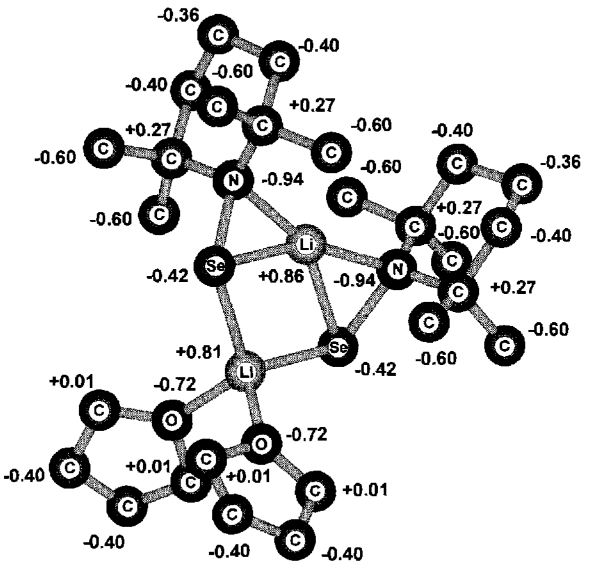
The partial charges derived from a natural bond orbital (NBO)[14] analysis (Figure 6) clearly support a predominantly electrostatic bonding model for this system which is already suggested by the shallowness of the deformation curve in the vicinity of the energy minimum. The NBO

Figure 5. Relative energy as a function of the coordination geometry around Li(1) (see text)



analysis also indicates a very substantial charge transfer from selenium (−0.42) to nitrogen (−0.94) which explains the overwhelming tendency for the observed chelating bonding mode and as a consequence the unique coordination geometry of Li(1). The lithium-nitrogen bond lengths are also entirely within the range found for lithium amides[5,8,9].

Figure 6. Atomic charges in **1** as calculated by NBO population analysis. Hydrogen atoms are not shown for clarity but bear an average charge of about +0.15



Recently the solution structure of PhSeLi was studied by multinuclear NMR techniques at −133 °C[15]. Depending on the solvent various forms of aggregations of CIP/SIP status could be detected. In ether, by observing a lithium-selenium coupling for the first time, a symmetric lithium bridged dimer was shown most likely to be present. Loss of coupling however occurs with addition of THF. Our attempts to decide if **1** and/or **2** are present in solution by $^{7}$Li- and $^{77}$Se-NMR spectroscopy at −33 °C were unsuccessful. Only bands without coupling pattern were observed, indicating exchange processes.

There is however a good reason for the exclusive crystallization of **1** out of solutions which might contain an equilibrium between **1** and **2**. The calculated dipole moment for **1** is 6.18 D in contrast to **2** which of course has no dipole moment. This large dipole moment leads to an enormous gain in lattice energy for the crystallization of **1** compared to **2**. Indeed the packing of **1** shows a three-dimensional head to tail arrangement.

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## Experimental Section

Reactions were carried out under argon and conventional Schlenk techniques were used. $^{77}$Se-NMR: Bruker WP 80, $^{7}$Li-NMR: Bruker AC 200.

*Lithium 2,2,6,6-tetramethylpiperidinoselenolate* (**1**): 10.0 mmol (1.49 g) of freshly destilled 2,2,6,6-tetramethylpiperidine was dissolved in 100 ml of dry THF and deprotonated by addition of 5.0 mmol methyllithium (1.6 M solution in hexane) at −78 °C. The mixture was then stirred for 2 h at −15 °C. After addition of 5.00 mmol (0.395 g) of oxygen-free elemental grey selenium at −55 °C, the reaction mixture immediately turned red. After dissolution of all selenium THF was removed under reduced pressure at −10 °C until about 5 ml of the reaction mixture was left. Then approximately 50 ml of cooled pentane (0 °C) was added. While the mixture was allowed to stand overnight at −20 °C extremely air- and moisture-sensitive, pale yellow crystals deposited, m.p. 70 °C (dec.). $^{77}$Se-NMR (80 MHz, THF, −33 °C): δ = 549 rel. $Me_2Se$[16]; $^{7}$Li-NMR (200 MHz, THF, −33 °C): δ = 1.08 rel. 0.3 M LiCl (aq); − $C_{26}H_{52}Li_2N_2O_2Se_2$ (596.51): calcd. C 52.35, H 8.79, N 4.69; found C 52.51, H 8.98, N 4.91.

*Crystal Structure Determination for compound* **1**: Pale yellow single crystals of **1** were obtained by crystallization from a mixture of THF and pentane at −20 °C. $C_{26}H_{52}Li_2N_2O_2Se_2$, formula weight 596.50 g/mol, monoclinic, $C2/c$ (No. 15), $a$ = 1788.4(4), $b$ = 1112.1(2), $c$ = 1564.0(3) pm, $\beta$ = 105.31(3)°, $V$ = 3.0002(10) nm$^3$, $Z$ = 4, $d_{\mathrm{calc.}}$ = 1.321 mg/cm$^3$. Diffractometer Siemens P4, Mo-$K_\alpha$ radiation (graphite monochromator, $\lambda$ = 71.073 pm), crystal size 0.4 × 0.2 × 0.2 mm$^3$, $T$ = 213(2) K, absorption coefficient $\mu$ = 2.488 mm$^{-1}$, $F(000)$ = 1248, ω scans (4.03 < Θ < 22.55). Intensities were measured for 1601 independent reflections of which 1176 were considered observed ($I \geq 2\sigma(I)$). Lorentz and polarization corrections were made. The structure was solved by direct methods, SHELXS-86, and refined by full matrix least-squares procedure on $F^2$ using SHELXL-93[17]. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were included in the refinement at calculated positions with isotropic temperature parameters. Convergence was obtained for 155 parameters with the agreement factors $R_1$ = 0.0464 and $R_w$ = 9.78 for 1176 reflections. Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-404234, the names of the authors, and the journal citation.

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