Preparation of LGe(Se)OH: A Germanium Analogue of a Selenocarboxylic Acid (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)

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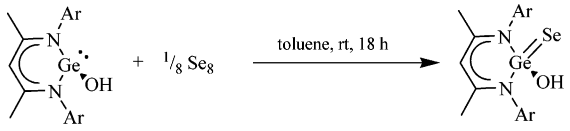
*Summary: LGe(Se)OH (**2**) (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$) was obtained by oxidative addition of red selenium to LGeOH (**1**). Compound **2** was characterized by IR, multinuclear NMR, EI-MS, and single-crystal X-ray diffraction. Furthermore, theoretical calculations of the acid strength (pK$_a$) of compound **2** and LGe(S)OH were carried out by means of density functional theory (DFT).*

Introduction

The chemical reactivity of heavier congeners of carbenes either as dicoordinate species or with higher coordination numbers is well documented.[1] To some extent steric and electronic stabilization apart from a proper synthetic route is a key factor in avoiding self-condensation and polymerization. For instance, the N-heterocyclic silylene 1,3-di-*tert*-butyl-2,3-dihydro-1*H*-1,2,3-diazasilol-2-ylidene in the presence of water leads to a transient silanol, which further self-condenses to the disiloxane.[2] A rare example of a hydroxygermylene compound, LGeOH (**1**) (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$), was recently synthesized and structurally characterized by our group.[3] The oxidative addition reaction of sulfur to the germanium center of **1** resulted in formation of LGe(S)OH.[4] The hydrogen abstraction from the hydroxyl group of **1** with metallocene-dimethyl derivatives of group 4 gave heterobimetallic oxides, LGe(μ-O)M(Me)Cp$_2$ (M = Zr, Hf).[5]

Scheme 1



1 Ar = 2,6-*i*Pr$_2$C$_6$H$_3$ **2**

The organic chemistry of selenium has received less attention than that of oxygen and sulfur.[6] However, studies of the chemistry of selenocarbonyl compounds are steadily increasing, leading to new synthetic approaches in a wide range of applications.[7] Although the existence of selenocarboxylic acids (RCSeOH) (R = alkyl, aryl) has been confirmed at low temperatures, structural evidence of such species has been elusive.[8] Furthermore, LGe(Se)Cl (L = HC[(CMe)(NAr)]$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, Ph) was used as a precursor to prepare LGe(Se)F and LGe(Se)(X) (X = Me, *n*Bu).[9] Herein, we report the preparation of LGe(Se)OH (**2**) by the reaction of **1** with elemental selenium.

Results and Discussion

Treatment of **1** in the presence of selenium in toluene at ambient temperature resulted in the oxidative addition of selenium to the germanium center, affording a germanium analogue of a selenocarboxylic acid in good yield (Scheme 1).

Compound **2** is thermally stable, decomposing above 200 °C. Its mass spectrum shows its molecular ion peak [M^+] with calculated isotopic pattern (m/z 586). The vibrational spectrum of **2** shows a broad absorption at 3299 cm^{-1} that is tentatively assigned to the OH group. LGe(S)OH showed the OH stretching frequency at lower wavenumber in comparison to **2** (3238 cm^{-1}).[4] In the ^{1}H NMR spectrum of **2** the OH proton resonance was observed at δ 2.19 ppm, which is downfield compared to that of **1** (δ 1.54 ppm).[3] However, it is shifted to high field

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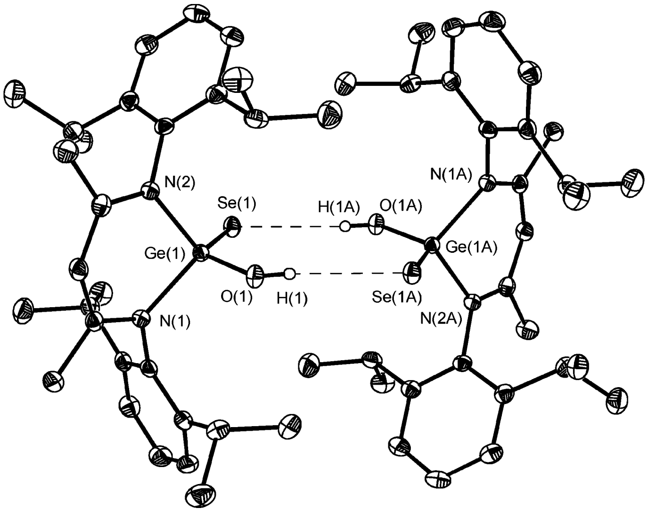

Figure 1. Thermal ellipsoid plot of **2** showing the 50% probability level. H atoms, except for the OH group and interstitial toluene molecule, are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ge(1)−O(1) 1.756(1), Ge(1)−Se(1) 2.206(1), O(1)−H(1) 0.76(2), Ge(1)−N(1) 1.915(1), Ge(1)−N(2) 1.912(1); N(2)−Ge(1)−N(1) 95.7(1), N(1)−Ge(1)−Se(1) 115.0(1), N(2)−Ge(1)−Se(1) 119.2(1), O(1)−Ge(1)−N(1) 102.0(1), O(1)−Ge(1)−N(2) 99.3(1), O(1)−Ge(1)−Se(1) 121.4(1), H(1)−O(1)−Ge(1) 112.5(2).

compared to that of LGe(S)OH (δ 2.30 ppm).[4] The ^{77}Se NMR resonance of **2** (δ −439 ppm) falls within the range of compounds exhibiting ylide-type and multiple-bond character at the germanium−selenium linkage: [LGe(Se)Cl L = HC-[(CMe)(NAr)]$_2$, Ar = 2,6-iPr$_2$C$_6$H$_3$, Ph, δ −287 ppm; LGe(Se)F δ −465 ppm, LGe(Se)(X), X = Me, nBu, δ −349 ppm, δ −297 ppm].[9]

Light green crystals of **2** were grown from a toluene/hexane solution (10:2 mL) at −20 °C for one week. Compound **2** crystallizes in the monoclinic space group $C2/c$ with one monomer and one molecule of toluene in the asymmetric unit. In **2**, a four-coordinate germanium atom occupies the center position of a distorted tetrahedron, which derives from the nitrogen atoms of the scaffold ligand, a hydroxyl group, and a selenium atom. Compound **2** prefers a selenoxo tautomeric form of hydrogen-bonded dimers, which derives from weak intermolecular hydrogen interactions (O−H···Se; O···Se 3.336(2)°, H···Se 2.61(2)°, O−H−Se 163(2)°). The structure of **2** is shown in Figure 1. The Ge−Se bond length (2.206(1) Å) in **2** is comparable with that reported for LGe(Se)Cl[1a,9] (2.197(6) Å, 2.210 Å), LGe(Se)F (av 2.174(7) Å), LGe(Se)(nBu) (2.219(6) Å),[9] and LGe(Se)Me (2.199(1) Å).[9] This is very much in line with resonance structure contributions between a Ge−Se ylide-type bond and multiple-bond character rather than a germanium−selenium single bond, whose bond distances range from 2.24 to 2.77 Å.[10,11] In **2** the Ge−O bond length (1.756(1) Å) remains nearly unchanged when compared with that of LGe(S)OH (1.751(2) Å).[4] A similar finding was also observed for **2**, having a Ge−N bond length of 1.914(1) Å (av), in good agreement with that of LGe(S)OH (av 1.914(2) Å),[4] as well as for that of LGe(Se)Cl (av 1.901(2) Å) and LGe(Se)F (av 1.887(3) Å).[9]

Scheme 2

$$\begin{tikzcd} BH_{(g)} \arrow[r] \arrow[d, "A"] & B^{-}_{(g)} \arrow[d, "C"] & + & H^{+}_{(g)} \arrow[d] \\ BH_{(aq)} \arrow[r] & B^{-}_{(aq)} & + & H^{+}_{(aq)} \end{tikzcd}$$

The acid strength of compounds **2** and LGe(S)OH were investigated by theoretical calculations using density functional theory (DFT) and making use of the depicted thermodynamic cycle (Scheme 2). The pK_a value can be calculated by the following formula:

$$\Delta G_{aq}{}^{0} = G^{0}(B_{gas}{}^{-}) + \Delta G_{solv}(B^{-}) + G^{0}(H_{gas}{}^{+}) + G_{solv}{}^{0}(H^{+}) - G^{0}(BH_{gas}) - \Delta G_{solv}{}^{0}(BH)$$

and

$$pK_a = \frac{\Delta G_{aq}{}^{0}}{2.303RT}$$

The resulting acid strengths of **2** (pK_a 38.3) and LGe(S)OH (pK_a 37.2) are weak. The pK_a values are in the range of aromatic (pK_a ∼33) and aliphatic (pK_a ∼48) compounds. However, when compared with oxygen-containing organic Brønsted acids (pK_a ∼15), they have weaker acid strength.[12] Likewise, these pK_a values correlate well when compared with the ^{1}H NMR resonances of the hydroxyl moiety of both compounds. Thus, compound LGe(S)OH can be regarded to be more acidic by virtue of its chemical shift and acid strength (δ 2.30 ppm; pK_a 37.2) when compared to those of **2** (δ 2.19 ppm; pK_a 38.3).

To further investigate the bonding situation around the germanium atom in **2** and LGe(S)OH compounds, a natural bond order analysis (NBO)[13−15] was carried out. The results of this analysis were also interpreted in terms of the donor−acceptor interaction.[16] As can be seen from the values given in Table 1, the Ge−S bond can be described in terms of the overlap between a p-rich sp-hybrid at the sulfur atom and a sp^2 hybrid of the germanium atom. The Ge−O bond also involves the overlap of two p-rich hybrids, but in this case the contribution of the germanium atom is far smaller. The Ge−N bonds show the same distribution. In addition, the Ge−S bond is further stabilized by 26 kcal/mol through the interaction of antibonding orbitals of the Ge−O and Ge−N bonds. The Ge−N bond forms part of a delocalized system with the germanium acting as bridging atom. In the case of compound **2** the analysis mostly differs at the Ge−Se bond, which shows a higher contribution of the germanium atom to the molecular orbital. The direct consequence of this electron drain is visible in the hydroxyl group,

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Table 1. Results of the Bonding Analysis of LGe(Ch)OH (1-S, Ch = S; 2-Se, Ch = Se)

	occ	bond	contr (%)	MO1	type	contr (%)	MO2	type
1-S	1.912	S−Ge	61.4	S	s(16%)p 5.2(83.7%)	38.6	Ge	s(34.2%)p 1.9(65.3%)
	1.965	Ge−O	16.2	Ge	s(23.5%)p 3.2(76.1%)	83.8	O	s(26.5%)p 2.7(73.5%)
	1.932	Ge−N5	15.6	Ge	s(21.3%)p 3.7(78.5%)	84.4	N5	s(27.8%)p 2.6(72.2%)
	1.932	Ge−N6	15.6	Ge	s(21.3%)p 3.7(78.5%)	84.4	N6	s(27.8%)p 2.6(72.2%)
	1.985	O−H	75.6	O	s(22.8%)p3.4(77.1%)	24.4	H	s(99.7%)
2-Se	1.903	Se−Ge	58.1	Se	s(14%)p 6.2(86%)	42	Ge	s(34%)p 1.9(65.4%)
	1.966	Ge−O	16.2	Ge	s(23.4%)p 3.3(76.3%)	83.8	O	s(27%)p 2.7(73%)
	1.933	Ge−N5	15.8	Ge	s(21.4%)p 3.7(78.3%)	84.2	N5	s(28.2%)p 2.6(71.8%)
	1.933	Ge−N6	15.8	Ge	s(21.4%)p 3.7(78.3%)	84.2	N6	s(28.2%)p 2.6(71.8%)
	1.985	O−H	75.6	O	s(22.6%)p 3.4(77.4%)	24.4	H	s(99.7%)

which now shows a positive interaction with the Ge−O bond, which was not visible in the sulfur system.

In summary, oxidative addition of selenium at the germanium center led to LGe(Se)OH. Also the first assessment of the acid strength of this new class of carbon-free carbonic acids based on germanium was carried out by density functional calculations.

Experimental Section

General Comments. All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. The solvents were purified according to conventional procedures and were freshly distilled prior to use. Red amorphous selenium was prepared according to the literature procedure.[17] NMR spectra were recorded on a Bruker Avance 500 instrument, and the ^{1}H, ^{13}C, and ^{77}Se chemical shifts are reported with reference to tetramethylsilane (TMS) and dimethylselenide (Me_2Se), respectively. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer. Mass spectra were obtained on a Finnigan MAT 8230 spectrometer by EI technique. Melting points were obtained in sealed capillaries on a Büchi B 540 instrument. CHN analyses were performed at the Analytical Laboratory of the Institut für Anorganische Chemie der Universität Göttingen, Germany.

Preparation of LGe(Se)OH (2). To a suspension of elemental red selenium (0.29 g, 3. 67 mmol) in toluene (20 mL) was added via cannula a solution of **1** (1.86 g, 3.67 mmol) in toluene (30 mL). A pale green solution appeared after 30 min, which finally remained unchanged after 18 h of stirring. Subsequent filtration and solvent removal gave a pale green solid, which was washed twice with cold pentane (2 × 10 mL). Yield: 1.66 g (77%). Mp: 220 °C dec. IR (KBr pellet): $\tilde{\nu} = 3292$ br (OH) cm^{-1}. ^{1}H NMR (500.13 MHz, C_6D_6, 25 °C, TMS): δ 7.09−7.16 (m, 6H; *m*-, *p*-Ar-*H*), 4.85 (s, 1H; γ-C*H*), 3.65 (sept, 2H, $^{3}J_{H-H} = 6.8$ Hz; C*H*(CH_3)$_2$), 3.29 (sept, 2H, $^{3}J_{H-H} = 6.8$ Hz; C*H*(CH_3)$_2$), 2.19 (s, 1H; O*H*), 1.56 (d, 6H, $^{3}J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.48 (s, 6H; C*H*$_3$), 1.30 (d, 6H, $^{3}J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.17 (d, 6H, $^{3}J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$), 1.04 ppm (d, 6H, $^{3}J_{H-H} = 6.8$ Hz; CH(C*H*$_3$)$_2$). ^{13}C NMR (125.75 MHz, C_6D_6, 25 °C, TMS): δ 169.6 (*C*N), 146.0, 144.7, 137.4, 129.0, 124.9, 124.7 (*i*-, *o*-, *m*-, *p*-*Ar*), 99.0 (γ-*C*H), 29.7 (*C*H$_3$), 28.0 (*C*H(CH_3)$_2$), 26.4 (*C*H(CH_3)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 23.8 ppm (CH(*C*H$_3$)$_2$). ^{77}Se NMR (95.38 MHz, C_6D_6, 25 °C, Me_2Se): δ −439.8 ppm. EI-MS (70 eV): [*m*/*z* (%)] 586 (35) [M^+], 571 (15) [$M^+ -$ Me], 553 (15) [$M^+ -$ MeOH], 507 (15) [$M^+ -$ Se]. Anal. Calcd for $C_{29}H_{42}GeN_2OSe$ (586.22): C, 59.42; H, 7.22; N, 4.78. Found: C, 59.18; H, 7.24; N, 4.66.

Molecular Structure Determination. Data for the structure of **2** was collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector with monochromated Cu Kα radiation ($\lambda = 1.54178$ Å). Intensity measurements were performed on a rapidly cooled crystal using ω scans. The structures were solved by direct methods (SHELXS-97)[18] and refined with all data by full-matrix least squares on F^2.[19] The hydrogen atom of compound **2** of the OH group was localized from the difference electron density map and refined isotropically, whereas the hydrogen atoms of C−H bonds were placed in idealized positions and refined isotropically with a riding model. The non-hydrogen atoms were refined anisotropically. Crystal data for compound **2**·toluene: $C_{36}H_{50}GeN_2OSe$, $M_w = 678.33$, monoclinic, space group $C2/c$, $a = 25.974(4)$ Å, $b = 16.195(3)$ Å, $c = 18.151(3)$ Å, $\beta = 115.82(3)°$, $V = 6873(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.311$ g·cm^{-3}, $F(000) = 2832$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, μ(Cu Kα) = 1.593 mm^{-1}. Of the 14 278 measured reflections, 4734 were independent [R(int) = 0.0210]. The final refinements converged at $R_1 = 0.0238$ for $I > 2\sigma(I)$, $wR_2 = 0.0620$ for all data. The final difference Fourier synthesis gave a min./max. residual electron density 0.391/−0.300 e·Å^{-3}.

Computational and Calculations Details. For all calculations the well-established DFT variant B3LYP method was used.[20,21] The computations were carried out with the Gaussian G03[22] program suite employing a modified 6-31G basis set extended with additional diffuse functions.[23,24] In the first step all molecules were fully optimized to their equilibrium structures. The resulting structures were in good agreement with the crystallographic data. To avoid the recourse to experimental data as much as possible, only the values for the proton have been taken from references.[25,26] The ab initio values for the energy of solvation (A,C) have been calculated with a modification of the polarizable continuum model (PCM) termed IEFPCM.[27]

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Supporting Information Available: X-ray data (CIF) for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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