Germanium Chemistry

Germacarboxylic Acid: An Organic-Acid Analogue Based on a Heavier Group 14 Element**

Leslie W. Pineda, Vojtech Jancik, Herbert W. Roesky, and Regine Herbst-Irmer*

Dedicated to Professor Jean-Marie Lehn on the occasion of his 65th birthday

Carbon multiple-bonded species, especially those containing carbonyl groups (aldehydes, amide esters, ketones) are widely known and useful systems in organic chemistry.[1] As far as the heavier congeners of Group 14 are concerned, a steady and remarkable development has been experienced, which includes the synthesis of unsaturated species. Additionally a myriad of mixed unsaturated compounds has been prepared containing elements of Groups 14–16.[2] However, owing to the high reactivity and tendency to polymerize these species have to be thermodynamically and kinetically stabilized.

In the case of germanium–chalcogen double-bonded species, a few thio-, seleno-, and telluroketones were prepared.[3] We have already reported the synthesis and structure of $[HC\{(CMe)(2,6\text{-}i\text{Pr}_2C_6H_3N)\}_2Ge(S)X]$[4] (X = Cl, F, $HC\{(CMe)(2,6\text{-}i\text{Pr}_2C_6H_3N)\}_2 = 2,6\text{-}i\text{Pr}_2C_6H_3NC(CH_3)CH\text{-}C(CH_3)NC_6H_3\text{-}2,6\text{-}i\text{Pr}_2$) with Group 14 and 16 elements

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[*] Dipl.-Chem. L. W. Pineda, Dipl.-Chem. V. Jancik,
Prof. Dr. H. W. Roesky, Dr. R. Herbst-Irmer
Institut für Anorganische Chemie
Universität Göttingen
Tammannstrasse 4, 37077 Göttingen (Germany)
Fax: (+49) 551-39-3373
E-mail: hroesky@gwdg.de

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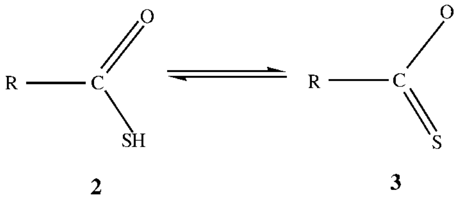
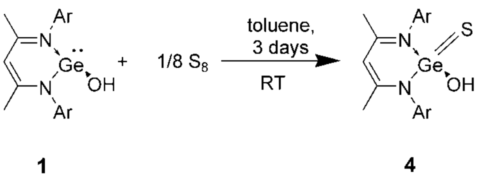
bearing a halide. Furthermore, the synthesis and structures of the selenium analogue $[HC\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2Ge(Se)X]$ (X = Cl, F), as well as the functionalized derivative $[HC\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2Ge(E)R]$ (E = S, Se; R = Me *n*Bu) were reported.[5] Recently, we succeeded in the isolation and structural characterization of the first terminal hydroxide based on germanium(II) $[HC\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2GeOH]$ (**1**).[6] As a stable precursor compound **1** is quite intriguing for the generation of new functional groups. To our knowledge the co-existence and fast tautomeric equilibrium for thiolocarboxylic acid **2** and thionocarboxylic acid **3** is known, but the latter group does not exist in the free state (Scheme 1).[7] Herein we report the first successful isolation and full characterization of a germanium thionoacid $[HC\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2Ge(S)OH]$ (**4**), which has no isolated precedent in the carbon system (see Scheme 2).



Scheme 1. Tautomeric equilibrium for the thiolo- and thionocarboxylic acid.

The reaction of **1** in the presence of equivalent amounts of elemental sulfur at room temperature in toluene leads after three days to the white compound **4** in moderate yield. (Scheme 2).



Scheme 2. Ar = 2,6-$iPr_2C_6H_3$.

Compound **4** is soluble in benzene, THF, and hexane, but insoluble in pentane and shows no decomposition on exposure to air. Compound **4** was fully characterized by IR, ^1H, and ^{13}C NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. By comparison of the IR spectrum of **1**, which exhibits a sharp OH stretching vibration at 3571 cm^{-1}[6] with the corresponding frequency of **4** (3238 cm^{-1}) a significant shift to lower wave numbers is observed. Such behavior may be due to the formation of hydrogen bonds. Interestingly, the ^1H NMR spectrum of **4** exhibits a resonance signal at $\delta = 2.30$ ppm for the hydroxy hydrogen, which by comparison with that of **1** ($\delta = 1.54$ ppm) clearly shows a downfield shift. Again intermolecular hydrogen interaction and a change of the oxidation state of the germanium atom are plausible explanations for the observed shift. Thus, this resonance shift indicates a fairly acidic nature of the terminal OH proton. Furthermore no evidence was found for any tautomeric equilibrium of **4**. The most abundant ion peak in the EI mass spectrum appeared at *m*/*z* 525 $[M{-}Me]^+$, and the signal at *m*/*z* 540 (40%) was assigned to the molecular ion $[M]^+$ (correct isotopic pattern).

Maintaining a toluene solution of **4** for two weeks at −20 °C, resulted in colorless single crystals suitable for X-ray structural analysis.[8] Compound **4** crystallizes in the monoclinic space group *C*2/*c*, with one monomer and one molecule of toluene in the asymmetric unit. Intermolecular interaction of the hydroxy group with the sulfur atom results in the formation of the hydrogen-bonding array (O–H···S) leading to dimers (Figure 1). The hydrogen bonded donor–acceptor separations (H···S, 2.537 Å and O···S 3.234 Å) follow the same trend as those reported in literature.[9] The coordination environment around the germanium atom comprises two nitrogen atoms from the supporting ligand, one hydroxy group, and one sulfur atom, and has a distorted tetrahedral geometry.

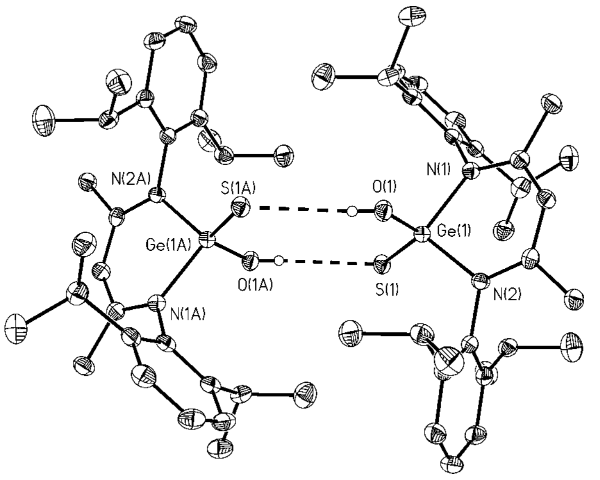


Figure 1. Thermal ellipsoid plot of **4** (thermal ellipsoids set at 50% probability). H atoms, except for the OH group, and interstitial toluene molecules, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ge(1)-O(1) 1.751(2), Ge(1)-N(2) 1.911(2), Ge(1)-N(1) 1.916(2), Ge(1)-S(1) 2.077(1); O(1)-Ge(1)-N(2) 99.6(1), O(1)-Ge(1)-N(1) 102.2(1), N(2)-Ge(1)-N(1) 95.6(1), O(1)-Ge(1)-S(1) 121.4(1), N(2)-Ge(1)-S(1) 118.8(1), N(1)-Ge(1)-S(1) 114.9(1).

The Ge–O bond length (1.751(2) Å) in **4** is significantly shorter than that in **1** (1.828(1) Å), as a result of the smaller atomic radius of Ge^{IV} compared with that of Ge^{II}. Indeed, similar Ge–O bond lengths for Ge^{IV} species have been described, $(tBu_2Ge(OH)_2$ (1.781(4) and 1.779(2) Å)[10] and 1.779(5) Å in $[(FcN)_3GeOH]$ (Fc = $CpFe(\eta^5\text{-}C_5H_4)$).[11] A shorter Ge–N bond length and wider N-Ge-N angle are expected (av. 1.914(2) Å and 95.6(1)°) than in **1**. A comparison of the Ge–S bond length in $[\{\eta^3\text{-}[(\mu\text{-}tBuN)_2(SiMe\,t\text{-}Bu)_2]\}GeS]$[12] (2.063(3) Å), and in $[HC\{(CMe)(2,6\text{-}iPr_2C_6H_3N)\}_2Ge(S)X]$[4] (X = Cl, F), (2.053(6) and 2.050(9) Å), with that in **4** (2.077(1) Å) shows a good agreement. Likewise, the Ge–O bond length in [(dppe)Pd(μ-S)(μ-

$CH_2O)Ge\{N(SiMe_3)_2\}_2]$ (dppe = bis(diphenylphosphanyl)-ethene)[13] (1.785(6) Å), a compound which has almost the same coordination environment and geometry at the germanium center as **4**, correlates well with that in **4**.

In summary the reaction of **1** and elemental sulfur resulted in the formation of the title compound **4** which represents a new class of "carbon-free" carbonic acid analogues based on germanium. The stability of **4** against oxygen and water at room temperature makes these systems quite interesting for biological investigations.

Experimental Section

All manipulations were performed under a dry and oxygen-free atmosphere (N_2 or Ar) by using Schlenk-line and glove-box techniques. Solvents were purified prior to use by distillation over appropriate drying agents in a nitrogen atmosphere.

4: A solution of **1** (1.56 g, 3.07 mmol) in toluene (30 mL) was slowly added to a suspension of elemental sulfur (0.09 g, 3.07 mmol) in toluene (15 mL) by cannula at room temperature. After 3 days under constant stirring at ambient temperature the yellow solution turned slightly green. After removal of all volatiles the remaining crude product was rinsed with pentane (3 × 10 mL) and dried under reduced pressure to yield pure **4**. Yield: 1.10 g (66 %); m.p. 300 °C (decomp); IR (KBr): $\tilde{\nu} = 3238$, 3063, 2965, 2867, 1638, 1539, 1442, 1388, 1322, 1257, 1175, 1102, 1023, 933, 875, 797, 712, 501 cm^{-1}; ^1H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 7.09–7.16$ (m, 6H, *m*-, *p*-Ar-H), 4.83 (s, 1H, γ-CH), 3.62 (sept, $^3J(H,H) = 6.8$ Hz, 2H, $CH(CH_3)_2$), 3.35 (sept, $^3J(H,H) = 6.8$ Hz, 2H, $CH(CH_3)_2$), 2.30 (s, 1H, OH), 1.57 (d, $^3J(H,H) = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.47 (s, 6H, CH_3), 1.26 (d, $^3J(H,H) = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.16 (d, $^3J(H,H) = 6.8$ Hz, 6H, $CH(CH_3)_2$), 1.05 ppm (d, $^3J(H,H) = 6.8$ Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (125.8 MHz, C_6D_6, 25 °C, TMS): $\delta = 169.9$ (C=N), 145.9, 144.9, 137.2, 128.9, 124.8, 124,6 (*i*-, *o*-, *m*-, *p*-, Ar), 98.5 (γ-CH), 29.5 (CH_3), 27.9 ($CH(CH_3)_2$), 26.3 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 23.8 ($CH(CH_3)_2$), 23.7 ppm ($CH(CH_3)_2$); EI-MS (70 eV): *m*/*z* (%): 540 (40) $[M]^+$, 525 (100) $[M-CH_3]^+$; elemental analysis (%) calcd for $C_{29}H_{42}GeN_2OS$ (539.32): C 64.59, H 7.85, N 5.19; found: C 64.20, H 7.57, N 5.12.

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[8] Crystal data for **4**·toluene: $C_{36}H_{50}GeN_2OS$, $M_r = 631.43$, monoclinic, space group *C*2/*c*, $a = 26.021(1)$, $b = 16.045(1)$, $c = 18.006(2)$ Å, $\beta = 114.79(1)°$, $V = 6825(1)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.229$ g cm^{-3}, $F(000) = 2688$, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $\mu(Cu_{K\alpha}) = 2.002$ mm^{-1}. Data for the structure were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector. Intensity measurements were performed on a rapidly cooled crystal (0.20 × 0.10 × 0.10 mm^3) in the range $6.66 \leq 2\theta \leq 118.08°$. Of the 21505 measured reflections, 4748 were independent $[R(int) = 0.0363]$. The structure was solved by direct methods (SHELXS-97)[14] and refined with all data by full-matrix least squares on F^2.[15] The hydrogen atoms of C–H bonds were placed in idealized positions, whereas the hydrogen atom from the OH moiety was localized from the difference electron-density map and refined isotropically. The final refinements converged at $R1 = 0.0283$ for $I > 2\sigma(I)$, $wR2 = 0.0730$ for all data. The final difference Fourier synthesis gave a min/max residual electron density −0.279/+0.355 e Å^{-3}. CCDC-240065 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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