APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 167–168
Main Group Metal Compounds
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.710

Crystallographic report

1-[4-(2-Thienyl)phenyl]germatrane

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Received 18 March 2004; Revised 18 April 2004; Accepted 19 May 2004

In the title compound, germanium is penta-coordinated and adopts a trigonal bipyramidal geometry. The (2-thienyl)phenyl group and the nitrogen atom each occupy an apical position with a transannular N→Ge bond distances of 2.247(4) and 2.219(4) Å for the two independent molecules. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: germatrane; synthesis; crystal structure; transannular N→Ge bond; toxicity

COMMENT

The title compound, 1-[4-(2-thienyl)phenyl]germatrane (**I**), a new representative of five-coordinated organogermanium compounds[1,2] with a heteroaromatic substituent at the central atom, has been investigated. The structure of **I** reveals that there are two non-equivalent molecules that differ from each other only marginally; one molecule is shown in Fig. 1. The germanium atom is penta-coordinated and trigonal bipyramidal; the deviation of the germanium atom from the trigonal plane is 0.263(1) Å in one molecule and 0.231(1) Å in the other. The (2-thienyl)phenyl group and the nitrogen atom each occupy an apical position. The transannular N→Ge bond is 2.247(4) Å in one molecule and 2.219(4) Å in the other. This bond is comparable to that in 1-phenylgermatrane,[2] 1-(4-methylphenyl)germatrane,[2] and 1-(4-bromophenyl)germatrane.[3] The deviation of germanium atom (ΔGe) from the O(2)–O(8)–O(9) plane in **I** is less expressed than in 1-phenylgermatrane [0.609(1) Å].[2] The introduction of the 2-thienyl substituent in the para-position of the aromatic ring lowers the acute toxicity of **I** (LD_{50} 324 mg kg^{-1}) about nine times in comparison with the unsubstituted phenylgermatrane (LD_{50} 35.5 mg kg^{-1})[2] and about five times in comparison with the *para*-methyl- or *para*-bromophenylgermatrane (LD_{50} 65.5 mg kg^{-1} and 70 mg kg^{-1} respectively).[2,3]

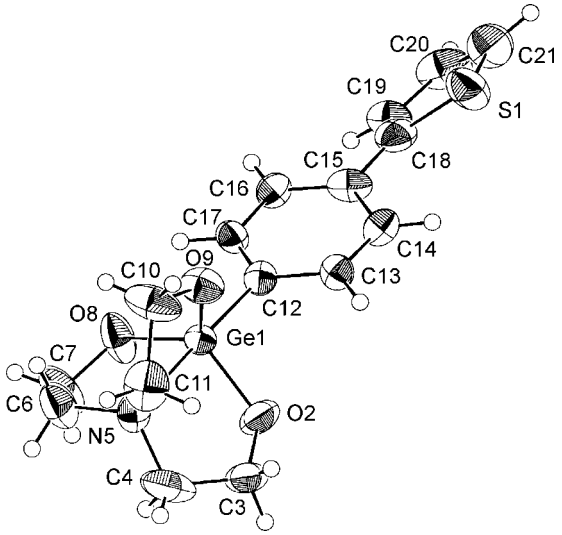

Figure 1. Molecular structure of one of the independent molecules in **I**. Key geometric parameters: Ge–O2 1.806(4), Ge–O8 1.798(3), Ge–O9 1.788(4), Ge–C12 1.948(5), O2–C3 1.432(7), O8–C7 1.397(6), O9–C10 1.420(7), C4–N5 1.454(7), Ge–N5 2.247(4), N5–C6 1.473(6), N5–C11 1.466(7) Å; O2–Ge–O8 114.9(2), O2–Ge–O9 117.6(2), O8–Ge–O9 121.2(2), O2–Ge–N5 81.0(2), O8–Ge–N5 81.72(15), O9–Ge–N5 81.8(2), C12–Ge–N5 178.9(2), C13–C12–Ge 121.3(4), O8–Ge–C12 99.0(2), C4–N5–C6 113.3(5), C4–N5–C11 115.2(5), C6–N5–C11 112.5(4)°.

EXPERIMENTAL

Synthesis

The mixture of 4-(2-thienyl)phenylbromide (0.75 ml, 0.003 mol) and the dioxane complex of $GeBr_2$ (1.6 g, 0.005 mol) in anhydrous toluene

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Contract/grant sponsor: Latvian Council of Science; Contract/grant number: 180.

(2 ml) was refluxed for 28 h under argon and from time to time analyzed by gas chromatography–mass spectrometry (GC–MS) (m/z, %): 472 (M^+, 20), 391 ($M^+ - Br$, 18), 238 (15), 153 (Ge − Br, 50) 115 (100), 89 (18). The resultant dark-yellow solution of 4-(2-thienyl)phenyltribromogermane (**II**) was transported to a three-necked flask under argon. An ethanolic solution (0.46 g, 0.01 mol) of triethylamine (1.06 g, 0.01 mol) in anhydrous Et_2O (1.5 ml) was added dropwise to **II**, cooled to 0 °C, followed by heating to room temperature, and boiling for 2 h. After cooling, the $Et_3N{\cdot}HCl$ was filtered off. Triethanolamine (0.49 g, 0.0033 mol) in ethanolic solution (1 ml) was added to the filtrate. The reaction mixture was stirred at room temperature for 1 h, cooled to 0 °C and germatrane **I** (0.10 g, 8.9%) was filtered off. Recrystallization from chloroform was carried out. The single crystals were grown from chloroform by slow evaporation of the solvent, m.p. 192–193 °C. Anal. Found: C, 50.57; H, 5.00; N, 3.64; S, 8.66. Calc. for $C_{16}H_{19}GeNO_3S$: C, 50.83; H, 5.07; N, 3.71; S, 8.48%. ^{1}H NMR (200 MHz, $CDCl_3$) δ ppm: 2.89 (6H, t, $N{-}CH_2$), 3.86 (6H, t, $O{-}CH_2$), 6.93–7.11 (3H, m, SC_4H_3), 7.44–7.77 (4H, m, C_6H_4). GC–MS (m/z, %): 379 (M^+, 70), 347 (10), 333 (10), 319 (25), 233 (10), 160 (100), 146 ($Ge[OCH_2CH_2]_3N$, 95), 127 (45), 115 (100), 102 (15), 89 (30), 70 (25), 56 (65), 42 (45). Intensity data for **I** were collected at 298 K on a Nonius KappaCCD diffractometer, using Mo Kα radiation for a colorless crystal 0.18 × 0.25 × 0.27 mm^3, $C_{16}H_{19}GeNO_3S$, $M = 377.99$, orthorhombic space group, $Pna2_1$, $a = 20.7296(4)$, $b = 6.6956(1)$, $c = 23.4483(5)$ Å, $V = 3254.56(11)$ Å^3, $Z = 8$, $\mu = 2.02$ mm^{-1}, 4188 unique data ($2\theta_{max} = 55.0°$), $R = 0.053$ (2268 reflections with $I > 3\sigma(I)$, $wR = 0.115$. In $Pna2_1$, to a first approximation the two ordered and independent molecules are related by an inversion center. However, the refinement of the crystal structures in the centrosymmetric space group leads to disordered atoms in the atrane cage with final R-factor of 0.078. Programs used: SIR97, maXus, ORTEP-II. CCDC deposition number: 231300.

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