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Crystallographic report

The crystal structure of 2-benzo[*b*]thienylgermatrane

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The germanium atom is penta-coordinated and adopts trigonal bipyramidal geometry. The 2-benzo[*b*]thienyl group and the nitrogen atom each occupy an apical position with the transannular N→Ge bond distance being 2.180(4) Å. Copyright © 2003 John Wiley & Sons, Ltd.

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

COMMENT

The title compound, 2-benzo[*b*]thienylgermatrane (**I**), is a new representative of five-coordinated organogermanium and organosilicon compounds[1,2] featuring fused heteroaromatic substituents at the central atom. The X-ray crystal structure of **I** reveals germanium to be penta-coordinated and trigonal bipyramidal; the deviation of the germanium atom from the trigonal plane is 0.1982(6) Å (Fig. 1). The 2-benzo[*b*]thienyl group and the nitrogen atom each occupy an apical position. The transannular N→Ge bond of 2.180(4) Å is comparable to those found in other hetarylgermatranes.[2–4]

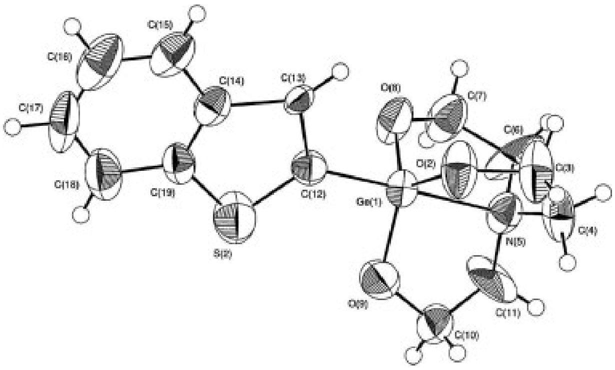

Figure 1. Molecular structure of **I**. Key geometric parameters: Ge(1)–O(2) 1.772(4), Ge(1)–O(8) 1.785(4), Ge(1)–O(9) 1.786(4), Ge(1)–C(12) 1.942(5), O(2)–C(3) 1.417(7), O(8)–C(7) 1.419(7), O(9)–C(10) 1.427(7), C(4)–N(5) 1.456(11), Ge(1)–N(5) 2.180(4), N(5)–C(6) 1.479(11), N(5)–C(11) 1.464(10) Å; O(2)–Ge(1)–O(8) 120.4(2), O(2)–Ge(1)–O(9) 117.9(2), O(2)–Ge(1)–N(5) 83.36 (19), O(8)–Ge(1)–O(9) 118.1(2), O(8)–Ge(1)–N(5) 83.70(18), O(9)–Ge(1)–N(5) 83.75(18), N(5)–Ge(1)–C(12) 178.75(19), Ge(1)–C(12)–C(13) 127.9(7)°.

EXPERIMENTAL

Synthesis

A mixture of 2-bromobenzo[*b*]thiophene (0.75 g, 0.0035 mol) and the dioxane complex of germanium(II) dibromide (1.12 g, 0.0035 mol) in 10 ml anhydrous toluene was refluxed for 167 h under argon atmosphere and from time to time analyzed by thin-layer chromatography. The resultant dark yellow solution of 2-benzo[*b*]thienyltribromogermane was transported to a three-neck flask under argon. An ethanolic solution (1 ml) of triethylamine (1.06 g, 0.01 mol) in anhydrous Et_2O (4 ml) was added dropwise to a 2-benzo[*b*]thienyltribromogermane, cooled to 0 °C, followed by heating to room temperature and boiling for 2 h. After cooling, the triethylamine salt was filtered off. Triethanolamine (0.52 g, 0.0035 mol) in ethanolic solution (1 ml) was added to the filtrate. The reaction mixture was stirred at room temperature for 2 h, cooled to 0 °C and germatrane **I** (0.13 g, 11%) was filtered off. Recrystallization was from chloroform. Single crystals were grown from a chloroform solution of **I** by slow evaporation of the solvent, m.p. 271–272 °C. Anal. Found: C, 47.56; H, 4.77; N, 3.94; S, 9.04. Calc. for $C_{14}H_{17}GeNO_3S$: C, 47.77; H, 4.87; N, 3.98; S, 9.11%. ^1H NMR (200 MHz, DMSO-d_6) δ ppm: 2.93 (6H, t, N–CH_2), 3.71 (6H, t, O–CH_2), 7.20–7.40 (2H, m, C_6H_4), 7.47 (1H, d, SC_4H), 7.73–7.96 (2H, m, C_6H_4).

Crystallography

Intensity data for **I** were collected at 293 K on a Nonius Kappa CCD diffractometer for a colorless crystal $0.10 \times 0.20 \times 0.25$ mm^3, $C_{14}H_{17}GeNO_3S$, $M = 351.94$, orthorhombic space group *Pbca*, $a = 11.0475(5)$, $b = 14.0543(5)$, $c = 18.8133(9)$ Å, $V = 2921.0(2)$ Å^3, $Z = 8$, 3333 unique data ($2\theta_{max} = 55°$), 2102 data with $I > 2\sigma(I)$, observed $R = 0.069$, $\omega R = 0.189$. Programs used: SHELXS-97, SHELXL-97. CCDC deposition number 202 776.

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REFERENCES

1. Lukevics E, Ignatovich L. Biological activity of organogermanium compounds. In *The Chemistry of Organic Germanium, Tin and Lead Compounds*, Rappoport Z (ed.). Wiley: 2002; 1651–1682.
2. Lukevics E, Ignatovich L, Belyakov S. *J. Organometal. Chem.* 1999; **588**: 222.
3. Lukevics E, Ignatovich L, Shul'ga T, Mitchenko O, Belyakov S. *J. Organometal. Chem.* 2002; **659**: 165.
4. Belyakov S, Ignatovich L, Lukevics E. *J. Organometal. Chem.* 1999; **577**: 205.