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Perchlorophenyl-germanium compounds. Crystal and molecular structure of perchlorotriphenylgermane

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Abstract

The synthesis of the first pentachlorophenyl derivatives of organo-germanium compounds, perchlorotriphenylgermane (**1**), tris(pentachlorophenyl)germane (**2**) and bromotris(pentachlorophenyl)germane (**4**), are reported; hydrolysis of **1** and **4** under neutral conditions gives tris(pentachlorophenyl)germanol (**3**). The structure of the germane **1** has been established by X-ray crystallography.

Introduction

To the best of our knowledge there has been no previous report of an arylgermanium compound containing a pentachlorophenyl group. We have now prepared some (pentachlorophenyl)germanes as part of a study of the synthesis and properties of pentachlorophenyl derivatives of group 4 elements. We have also determined the crystal structure of the very crowded perchlorotriphenylgermane (**1**). In the account below the Cl_5C_6 group is denoted by Ph_{Cl} .

Results and discussion

By far, the most versatile route to polyarylgermanium compounds involves the reaction of an organochlorogermane with the appropriate aryl-lithium or -magnesium reagent [1]. Thus perchlorotriphenylgermane (**1**) is readily prepared by the reaction of tetrachlorogermane with pentachlorophenyllithium (prepared from hexachlorobenzene and *n*-butyllithium [2]) in diethyl ether (Scheme 1). Hydrolysis of the germane **1** under basic conditions involves cleavage of the $\text{Ph}_{\text{Cl}}\text{-Ge}$ bond, yielding pentachlorobenzene as the sole organic compound, but under neutral

Table 1

Bond distances (Å) and bond angles (°) with their e.s.d.'s

Ge(1)–Cl(1)	2.158(s)	C(2)–Ge(1)–Cl(1)	105.6(2)	C(11)–C(10)–Cl(10)	118.0(6)
C(2)–Ge(1)	1.982(7)	C(8)–Ge(1)–Cl(1)	100.4(2)	C(11)–C(10)–C(9)	120.5(8)
C(8)–Ge(1)	1.976(7)	C(8)–Ge(1)–C(2)	116.3(3)	C(10)–C(11)–Cl(11)	120.6(7)
Cl(4)–Ge(1)	1.972(7)	C(14)–Ge(1)–Cl(1)	111.8(2)	C(12)–C(11)–Cl(11)	120.8(7)
C(3)–Cl(3)	1.710(7)	C(14)–Ge(1)–C(2)	105.8(3)	C(12)–C(11)–C(10)	118.5(7)
C(4)–Cl(4)	1.715(7)	Cl(4)–Ge(1)–C(8)	116.6(3)	C(11)–C(12)–Cl(12)	119.3(7)
C(5)–Cl(5)	1.699(7)	C(3)–C(2)–Ge(1)	124.895	C(13)–C(12)–Cl(12)	120.5(7)
C(6)–Cl(6)	1.708(7)	C(7)–C(2)–Ge(1)	118.2(5)	C(13)–C(12)–C(11)	120.1(8)
C(7)–Cl(7)	1.734(7)	C(7)–C(2)–C(3)	116.9(6)	C(8)–C(13)–Cl(13)	120.6(6)
C(9)–Cl(9)	1.718(7)	C(2)–C(3)–Cl(3)	121.3(5)	C(12)–C(13)–Cl(13)	117.4(6)
C(10)–Cl(10)	1.738(8)	C(4)–C(3)–Cl(3)	118.0(5)	C(12)–C(13)–C(8)	122.0(8)
C(11)–Cl(11)	1.713(8)	C(4)–C(3)–C(2)	120.6(6)	C(15)–C(14)–Ge(1)	127.4(7)
C(12)–Cl(12)	1.716(9)	C(3)–C(4)–Cl(4)	120.0(6)	C(19)–C(14)–Ge(1)	116.9(6)
C(13)–Cl(13)	1.723(8)	C(5)–C(4)–Cl(4)	118.8(6)	C(19)–C(14)–C(15)	115.3(8)
C(15)–Cl(15)	1.673(11)	C(5)–C(4)–C(3)	121.2(6)	C(14)–C(15)–Cl(15)	120.4(8)
C(16)–Cl(16)	1.699(11)	C(4)–C(5)–Cl(5)	121.4(6)	C(16)–C(15)–Cl(15)	118.4(8)
C(17)–Cl(17)	1.742(11)	C(6)–C(5)–Cl(5)	119.7(5)	C(16)–C(15)–C(14)	120.9(10)
C(18)–Cl(18)	1.703(11)	C(6)–C(5)–C(4)	118.9(6)	C(15)–C(16)–Cl(16)	120.1(11)
C(19)–Cl(19)	1.724(9)	C(50)–C(6)–Cl(6)	118.8(5)	C(17)–C(16)–Cl(16)	120.5(11)
C(3)–C(2)	1.418(10)	C(7)–C(6)–Cl(6)	122.4(6)	C(17)–C(16)–C(15)	119.0(10)
C(7)–C(2)	1.392(9)	C(7)–C(6)–C(5)	118.8(6)	C(16)–C(17)–Cl(17)	119.7(11)
C(4)–C(3)	1.398(10)	C(2)–C(7)–Cl(7)	119.8(6)	C(18)–C(17)–Cl(17)	118.0(11)
C(5)–C(4)	1.383(10)	C(6)–C(7)–Cl(7)	116.5(5)	C(18)–C(17)–C(16)	122.2(10)
C(6)–C(5)	1.427(10)	C(6)–C(7)–C(2)	123.6(6)	C(17)–C(18)–Cl(18)	121.8(9)
C(7)–C(6)	1.379(10)	C(9)–C(8)–Ge(1)	118.8(5)	C(19)–C(18)–Cl(18)	121.8(9)
C(9)–C(8)	1.402(10)	C(13)–C(8)–Ge(1)	124.3(6)	C(19)–C(18)–C(17)	116.4(10)
C(13)–C(8)	1.390(10)	C(13)–C(8)–C(9)	116.8(7)	C(14)–C(19)–Cl(19)	118.3(6)
C(10)–C(9)	1.356(11)	C(8)–C(9)–Cl(9)	120.1(6)	C(18)–C(19)–Cl(19)	115.9(7)
C(11)–C(10)	1.410(12)	C(10)–C(9)–Cl(9)	117.9(6)	C(18)–C(19)–C(14)	125.7(9)
C(12)–C(11)	1.379(12)	C(10)–C(9)–C(8)	122.0(7)	C(22)–C(21)–C(20)	148.2(26)
C(13)–C(12)	1.386(11)	C(9)–C(10)–Cl(10)	121.5(7)		
C(15)–C(14)	1.405(11)				
C(19)–C(14)	1.381(11)				
C(16)–C(15)	1.417(16)				
C(17)–C(16)	1.368(17)				
C(18)–C(17)	1.377(17)				
C(19)–C(18)	1.385(12)				
C(21)–C(20)	1.272(25)				
C(20)–C(20)	1.408(32)				
C(22)–C(21)	1.344(23)				

chlorophenyl group. The three Ge–C bond distances are similar (ca. 1.98 Å), and Ge–Cl is 2.158(2) Å; all of these distances are close to the average literature values. The Cl–Ge–C bond angles are 105.6(2), 100.4(2) and 111.8(2)° and the C–Ge–C are 116.3(3), 116.6(3) and 105.8(3)°, and reveal a considerable distortion of the tetrahedral environment around the Ge atom.

The conformation of the three pentachlorophenyl rings can be described in terms of the torsion angles between the Cl–Ge–C planes and the corresponding mean planes of the phenyl rings, namely ϕ_1 (52.6°), ϕ_2 (62.9°) and ϕ_3 (15.4°), which indicate a conformation which departs from ideal C_3 symmetry group [6]. The conformation differs substantially from that of perchlorotriphenylsilane [7] because

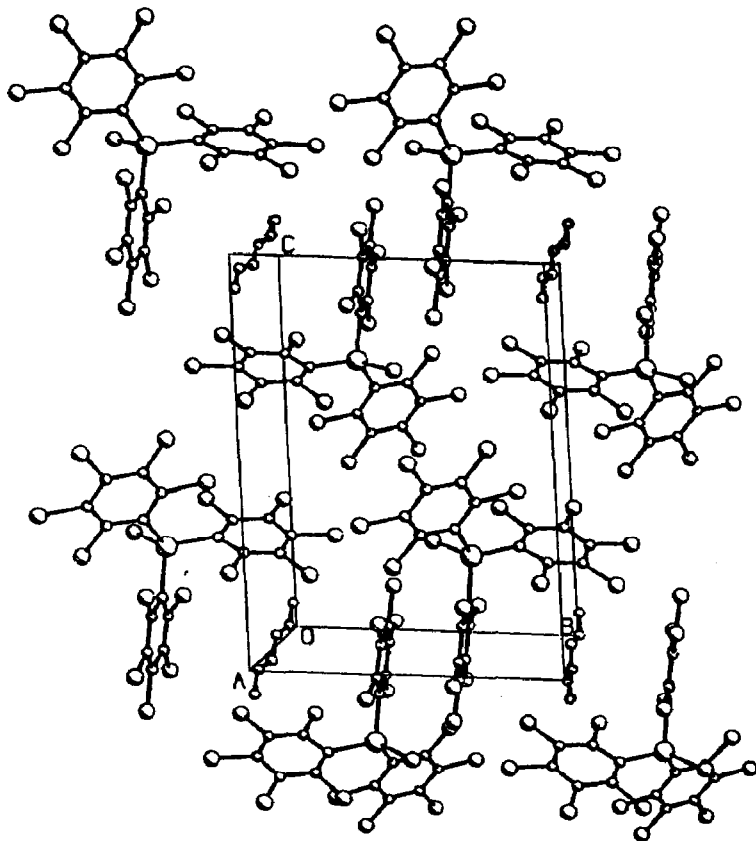


Fig. 2. Perspective view of the unit cell, illustrating the molecular packing in the solvated (n-hexane) form of 1.

of the longer bond distances between phenyl rings and the central atom. This allows a greater degree of freedom in the disposition of the phenyl rings. The close packing of the crystal involves strong intermolecular interactions which may be the origin of the irregular conformation. The shortest intermolecular contacts are Cl(18)...Cl(9)ⁱ, 3.343 Å, ($i = x, -1 + y, z$) and C(11)...Cl(15)ⁱⁱ, 3.316 Å ($ii = -1 + x, y, z$). We also note that, in spite of the presence of the interstitial hexane molecules (Fig. 2), the density remains high, and the closeness of the packing is also reflected in the high m.p. (294°C).

Experimental

Solvents and reagents were dried and purified by standard methods. Melting points were determined with a Kofler microscope. Infrared spectra were recorded on Perkin-Elmer 682 and 1330 spectrometers. All UV spectra were recorded on a Beckmann Acta M-VI. Mass spectral data were obtained with a double focusing AEI M5-9025 instrument (70 eV, 100 μ A emission).

Perchlorotriphenylgermane (1)

(a) *Preparation.* A solution of germane tetrachloride (1.37 g; 6.4 mmol) in diethyl ether (20 ml) was added dropwise during 30 min to a stirred solution of

Table 2

Fractional atomic coordinates ($\times 10^4$) with their e.s.d.'s and their equivalent isotropic temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	Beq
Ge(1)	2773(1)	2995(1)	7331(1)	3.15
Cl(1)	4464(2)	4425(2)	7139(1)	4.68
Cl(3)	-692(2)	3027(2)	8234(1)	4.58
Cl(4)	-828(2)	3458(2)	10152(1)	5.27
Cl(5)	2204(3)	3802(2)	11398(1)	5.34
Cl(6)	5418(2)	3628(2)	10719(1)	4.76
Cl(7)	5628(2)	3103(2)	8804(1)	4.51
Cl(9)	1060(3)	5392(2)	7510(2)	5.23
Cl(10)	-1695(3)	6029(2)	6307(2)	6.91
Cl(11)	-2994(3)	4333(3)	4725(2)	7.66
Cl(12)	-1597(4)	1950(3)	4394(2)	7.93
Cl(13)	1143(4)	1283(2)	5575(2)	6.76
Cl(15)	5991(6)	2254(4)	6334(4)	15.46
Cl(16)	7188(4)	-202(5)	6358(4)	13.97
Cl(17)	5315(6)	-2211(3)	7130(3)	12.07
Cl(18)	2230(6)	-1732(2)	7872(2)	9.93
Cl(19)	981(3)	671(2)	7769(2)	6.35
C(2)	2486(8)	3171(6)	8558(4)	3.16
C(3)	1027(8)	3242(6)	8887(5)	3.34
C(4)	950(9)	3414(7)	9764(5)	3.78
C(5)	2290(8)	3562(6)	10333(4)	3.51
C(6)	3766(8)	3467(7)	10014(5)	3.38
C(7)	3810(8)	3274(6)	9147(5)	3.4
C(8)	989(9)	3333(6)	6533(5)	3.51
C(9)	332(9)	4405(6)	6661(5)	3.76
C(10)	-861(10)	4712(7)	6124(6)	4.47
C(11)	-1492(11)	3946(9)	5409(6)	5.15
C(12)	-841(11)	2898(9)	5259(5)	5.12
C(13)	378(10)	2600(7)	5814(5)	4.31
C(14)	3590(9)	1446(7)	7135(5)	3.99
C(15)	4983(11)	1210(9)	6794(7)	6.37
C(16)	5484(12)	58(14)	6758(8)	7.81
C(17)	4668(16)	-806(10)	7128(8)	7.32
C(18)	3285(14)	-628(8)	7460(7)	6.08
C(19)	2796(10)	496(7)	7440(5)	4.43
C(20)	3282(24)	-13(16)	258(15)	13.30
C(21)	2889(30)	219(19)	348(16)	17.57
C(22)	1798(20)	191(16)	832(14)	13.51

pentachlorophenyllithium (prepared from hexachlorobenzene (7.0 g, 24.6 mmol) and *n*-BuLi (1.47 *M* in hexane) (16 ml; 23.6 mmol) in diethyl ether (100 ml)) at 0 °C. The mixture was allowed to warm to room temperature and stirring was continued at that temperature for 1 h, and the mixture was then refluxed for 15 h. The solvent was removed by distillation with exclusion of moisture, benzene (90 ml) was added to the residue and the mixture was boiled for 2 h to facilitate dissolution of the organic material. The insoluble material was filtered off. The filtrate was evaporated to dryness and the residue chromatographed on a column (silica gel with hexane as eluant) and then low molecular weight components (a mixture of hexachlorobenzene

and pentachlorobenzene, 0.8 g) were sublimed off. The residue was perchlorotriphenylgermane (4.4 g; 80%), m.p. 294–296 °C (from hexane). IR(KBr) 1512(m), 1335(s), 1325(s), 1300(s), 1215(w), 1195(w), 1170(m), 1085(m), 850(s), 705(w), 675(s) cm^{-1} . IR (polyethylene-Nujol) 395(m), 355(w), 270(m) cm^{-1} . UV-vis (CHCl_3) 290 (sh) nm, 301, 311 (ϵ 1530, 3080, 3750). Mass spectrum: m/z 856 (33%, M^+), 821 (32.5, $(\text{C}_6\text{Cl}_5)_3\text{Ge}^+$), 607 (100, $(\text{C}_6\text{Cl}_5)_2\text{GeCl}^+$), 570 (39, $(\text{C}_6\text{Cl}_5)_2\text{Ge}^+$). Anal. Found: C, 25.5; Cl, 66.4. $\text{C}_{18}\text{Cl}_{16}\text{Ge}$ calcd.: C, 25.3; Cl, 66.3%.

(b) *Crystal data.* $\text{C}_{18}\text{Cl}_{16}\text{Ge} \cdot 0.5 \text{C}_6\text{H}_{14}$, $M = 899.6$, triclinic, a 8.638(2), b 11.419(1), c 15.483(3) Å, α 94.40(1), β 95.80(2), γ 94.77(1)°, V 1543.6 Å³, $Z = 2$, D_c 1.93 Mg m^{-3} , space group $P\bar{1}$, well-formed colourless crystals, $0.23 \times 0.32 \times 0.36$ mm, $\mu(\text{Mo-K}_\alpha)$ 23.9 cm^{-1} .

(c) *Intensity data, structure solution and refinement.* Intensity data were collected on an Enraf–Nonius CAD4 diffractometer over the range $1 < \theta < 25^\circ$. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using MULTAN 11/84 [4] and refined by full-matrix least-squares technique with SHELX-76 [5] to $R = 0.059$ and $R_w = 0.066$ where $w = 1/(\sigma^2(F) + 0.000879F^2)$ for 3790 observed reflections ($I > 2.5\sigma(I)$). The atomic parameters are given in Table 1.

Tris(pentachlorophenyl)germane (2).

A solution of LiAlH_4 (64 mg) in diethyl ether (20 ml) was added slowly at room temperature to a stirred mixture of perchlorotriphenylgermane (1.43 g) in diethyl ether (50 ml). The mixture was stirred for 3 h, then an excess of dilute hydrochloric acid was added and the mixture then extracted with chloroform. The extract was dried over Na_2SO_4 then evaporated, and the residue was chromatographed on silica gel (with hexane as eluant) to give tris(pentachlorophenyl)germane (1.2 g; 88%), m.p. 248–249° (from benzene/hexane). IR (KBr) 2180(w), 1515(m), 1340(s), 1325(s), 1300(s), 1220(w), 1200(w), 1165(m), 1085(m), 850(s), 765(s), 740(s), 700(w), 675(s) cm^{-1} . UV-vis (CHCl_3) 285(sh) nm, 294, 304 (ϵ 1280, 2290, 2600). Anal. Found: C, 26.2; H, 0.1; Cl, 64.4. $\text{C}_{18}\text{HCl}_{15}\text{Ge}$ calcd.: C, 26.3; H, 0.1; Cl, 64.7%.

Bromotris(pentachlorophenyl)germane (4).

A solution of bromine (0.145 g; 0.91 mmol) and tris(pentachlorophenyl)germane (0.7 g; 0.85 mmol) in CCl_4 (50 ml) was refluxed in the dark with exclusion of moisture for 24 h and then evaporated to dryness under vacuum. The residue was washed many times with CCl_4 and purified by column chromatography (silica gel, with CCl_4 as eluant) to give bromotris(pentachlorophenyl)germane (0.71 g; 93%), m.p. 292–293° (from CCl_4 /hexane). IR (KBr) 1510(m), 1335(s), 1320(s), 1295(s), 1215(w), 1200(w), 1170(m), 1155(w), 1085(m), 850(s), 710(w), 680(s) cm^{-1} . IR (polyethylene/Nujol) 390(w), 355(w), 285(m), 265(m) cm^{-1} . UV-vis (CHCl_3) 298(sh) nm, 301, 311 (ϵ 1470, 2960, 3540). Mass spectrum: m/z 900 ($< 0.5\%$, M^+), 821 (100, $(\text{C}_6\text{Cl}_5)_3\text{Ge}^+$), 570 (23, $(\text{C}_6\text{Cl}_5)_2\text{Ge}^+$). Anal. Found: C, 24.4; H, 0.2; Br, 8.5; Cl, 59.1. $\text{C}_{18}\text{BrCl}_{15}\text{Ge}$ calcd.: C, 24.0; H, 0; Br, 8.9; Cl, 59.1%.

Neutral hydrolysis of 1 and 4. Tris(pentachlorophenyl)germanol (3)

(a) *From perchlorotriphenylgermane (1).* A solution of 1 (0.10 g) in tetrahydrofuran/water (1/1) (20 ml) was refluxed for 5 h and then extracted with chloroform. The extract was dried over Na_2SO_4 then evaporated under vacuum to leave

tris(pentachlorophenyl)germanol (83 mg; 85%), m.p. 271–273 °C (from chloroform). IR (KBr) 3620(m), 1515(m), 1340(s), 1325(s), 1300(s), 1215(w), 1200(w), 1170(m), 1160(m), 1085(s), 940(s), 855(s), 710(w), 690(s), 680(s) cm^{-1} . UV-vis (CHCl_3) 288(sh) nm, 297, 307 (ϵ 1540, 2725, 3175). Anal. Found: C, 26.0; H, 0.1; Cl, 63.7. $\text{C}_{18}\text{HCl}_{15}\text{OGe}$ calcd.: C, 25.8; H, 0.1; Cl, 63.5%.

(b) From bromotris(pentachlorophenyl)germane (**4**). A similar procedure but with **4** gave the corresponding tris(pentachlorophenyl)germanol (87%).

Reaction of **3** with SOCl_2

A solution of tris(pentachlorophenyl)germanol (0.12 g) in thionyl chloride (10 ml) was heated under reflux for 3 h with exclusion of moisture and then evaporated to dryness to give perchlorotriphenylgermane (0.12 g; 99%), identical (IR and m.p.) with the sample described above.

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