Synthesis and characterization of trichlorogermyl dioic acids: crystal structures and complementary hydrogen bonding motifs in 3-(trichlorogermyl) pentanedioic acid and 2-[(trichlorogermyl)methyl]butanedioic acid

Sumera Mahboob[1], Rohama Gill[1], Muhammad Mazhar[1], Gabriele Kociok-Köhn[2], Kieran C. Molloy[2]

[1] Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan
[2] Department of Chemistry, University of Bath, Bath, UK

Abstract A series of trichlorogermyl-substituted dicarboxylic acids of general formula $HOOC–R'–COOH$ where $R' = –CH_2CH(GeCl_3)CH_2–$ **1**, $–CH(CH_2GeCl_3)CH_2–$ **2**, $–CH(GeCl_3)CH_2–$ **3** and $–CH(CH_3)CH(GeCl_3)–$ **4** were synthesized by the hydrogermylation reaction of unsaturated acids, such as *trans*-glutaconic (2-pentenedioic acid), itaconic (methylenebutanedioic acid), fumaric (2-butenedioic acid), and citraconic (2-methyl-2-butenedioic acid) acids with $HGeCl_3$, which was produced *in situ* by the reaction of GeO_2 with 37% HCl in presence of $NaH_2PO_2 \cdot H_2O$. All these compounds were characterized by melting point, CHN analysis, FTIR, and multinuclear NMR (^{1}H; ^{13}C; H,H-COSY). X-Ray crystal structures of **1** and **2** were analyzed to show supramolecular structures in which central Ge atom in each of these structures is four-coordinated with a slightly distorted tetrahedral geometry. Structurally, both compounds adopt supramolecular forms *via* strong intermolecular O–H–O interactions through 8-membered and 22-membered hydrogen bonded rings.

Keywords Hydrogermylation; Crystal structure; Supramolecules; Hydrogen bonding.

Correspondence: Muhammad Mazhar, Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan.
E-mail: mazhar42pk@yahoo.com

Introduction

Trichlorogermane has been reported in literature for the preparation of a variety of carbofunctional organogermanium compounds with valuable biological activity [1]. The presence of Ge–Cl bonds, and in some instances also of multiple carbon–carbon bonds, enable these compounds to undergo various chemical reactions and modifications such as alkylation, arylation, hydrolysis, co-hydrolysis, cross-linking, vulcanization and polymerization [2]. Trichlorogermane reacts with various unsaturated carboxylic acids at elevated temperature in absence of either catalyst or an initiator to give hydrogermanated products [3]. We have found that these C-germyl-mono- [4, 5] and di-carboxylic acids exist in dimer and supramolecular forms with strong intermolecular hydrogen bonding, rather than heterochain polymers containing germanium in their backbone.

These results and literature data led us to investigate the related hydrogermylation reaction of some more unsaturated dicarboxylic acids and the structural nature of the reaction products in which their molecular aggregates become organized with the help of strong and directional intermolecular interactions. Functional groups such as carboxyl, amide, and alcohol have often been explored to evaluate their influence on the hydrogen bonding modes of carboxylic acids, however, in contrast the influence

of peripheral metal-based moieties have been largely overlooked. Herein, we describe hydrogermylation reaction of various unsaturated dicarboxylic acids and report crystal structures of 3-(trichlorogermyl)-pentanedioic acid **1** and 2-[(trichlorogermyl)methyl]butanedioic acid **2** in order to assess the extent to which the symmetry of the acid influences the construction of a hydrogen bonded lattice.

Results and discussion

Trichlorogermyl derivatives of *trans*-glutaconic (2-pentenedioic acid), itaconic (methylenebutanedioic acid), fumaric (2-butenedioic acid), and citraconic (2-methyl-2-butenedioic acid) acids have been prepared in 63–79% yield by hydrogermylation reaction of respective organic acid with $HGeCl_3$ in a one pot reaction using standard literature method (Scheme 1) [6]. All these compounds are white crystalline solids, stable at room temperature except **3** and **4** which need inert atmosphere and soluble in *Me*OH and *DMSO*.

The case of addition of R_3GeH (where R = organic sample or a halide) to C=C mainly depends on the

GeO$_2$ + NaH$_2$PO$_2$·H$_2$O + HCl (37%) + H$_2$O
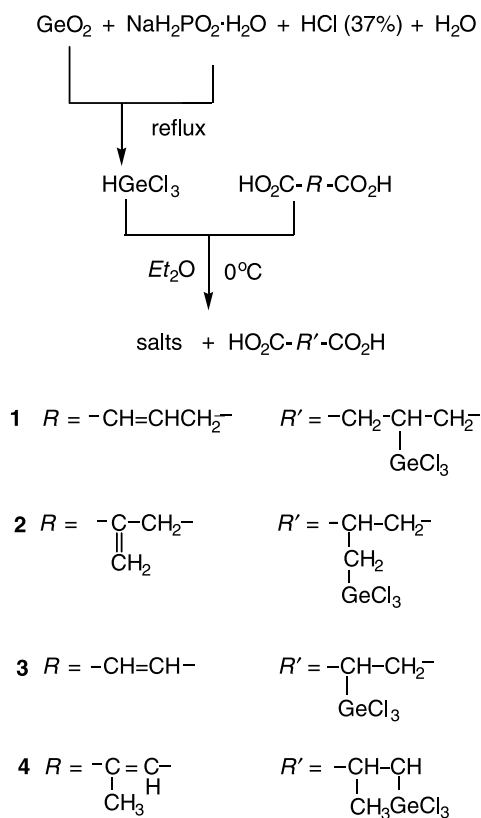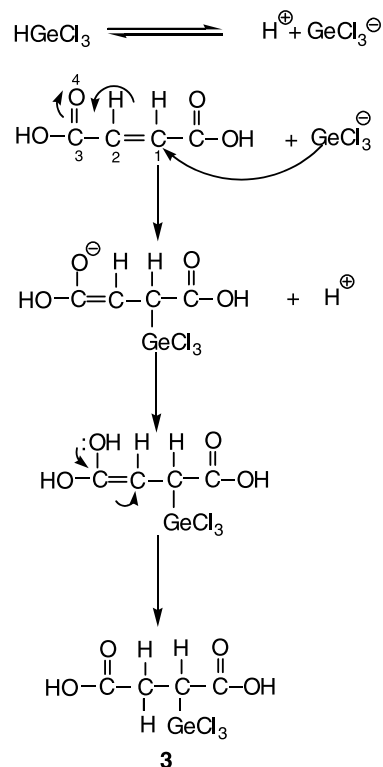
Scheme 1

Scheme 2

polarity of Ge–H bond [7], reagent structure [8], catalyst [9], and the solvent [10]. The stereospecificity of hydrogermylation has been studied in the case of alkenes and alkynes and these reactions generally occurred with retention of configuration on the metal [11]. Our studies on hydrogermylation reactions of unsaturated dicarboxylic acids clearly indicate the reaction to proceed *via* 1,4-*Michael* addition yielding a single regioselective product as shown in Scheme 2.

FTIR spectra of all trichlorogermyl dicarboxylic acids **1**–**4** showed a strong and broad band for O–H in the region of $\bar{\nu} = 3300$–$3200\,cm^{-1}$ indicating the presence of hydrogen bonding in carboxylic acids. The ν_{asym} and ν_{sym} of C=O stretching appeared in the range of $\bar{\nu} = 1700$–1729 and $1255\,cm^{-1}$ respectively. Other vibrations such as Ge–C and Ge–Cl have been located in the region $\bar{\nu} = 580$–$589\,cm^{-1}$ and 422–$425\,cm^{-1}$ respectively [12, 13].

The NMR chemical shifts for **1**–**4** were assigned by comparison with the spectra of parent acids and earlier publications [4, 5]. The compounds **2**–**4** contain a chiral center and more than one in case of **4**. In the case of **2** the two prochiral CH$_2$ centers holding two pairs of diastereotopic protons were observed as
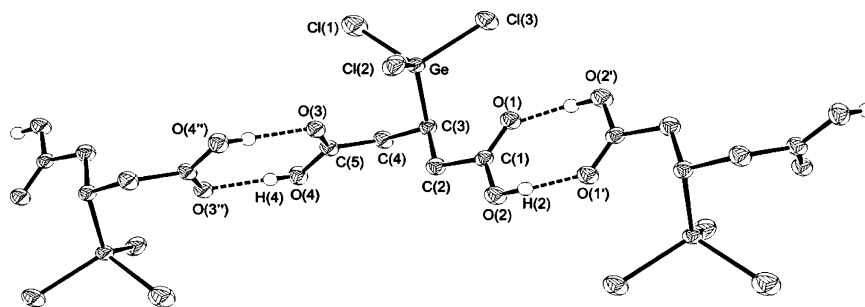
Fig. 1 A view of molecule **1** with displacement ellipsoids plotted at the 30% probability level. Symmetry operations: $'1 - x$, $-y, -z$; $''-x, 1 - y, -z$

multiplets rather than true ABX pattern. In compound **3** the CHGe is a chiral center, the CH_2 is a prochiral center, and the three protons in the CH_2CHGe unit gave two multiplets in the region $\delta = 2.16–2.33$ ppm.

^{13}C NMR data for **1**–**4** are presented in the experimental section. These data confirm the formation of only a single regioselective product in each case [6]. The carbonyl carbons in **1** have the same chemical environment, as such they show a single peak at $\delta = 172.5$ ppm, whereas in **2**, **3** and **4** the carbonyl carbons show two different peaks. The presence of $GeCl_3$ shifts one carbonyl peak slightly upfield in **2**, **3** and **4** [13].

Fig. 2 The lattice structure of **1**

The crystal data for **1** and **2** are given in Table 1. The asymmetric units of **1** and **2** are shown in Figs. 1–4. The central Ge atom in each compound is four-coordinate with distorted tetrahedral geometry, having Cl–Ge–Cl angles in the range 101.90(2)–107.15(2)° in **1** and 102.70(2)–106.31(2)° in **2**. The Ge $-$ C$_{sp^3}$ distance in **1** (Ge–C3, 1.9626(16) Å) is little longer than in **2** (Ge–C1, 1.9374(19) Å). Of

Table 1 Crystallographic data for **1** and **2**

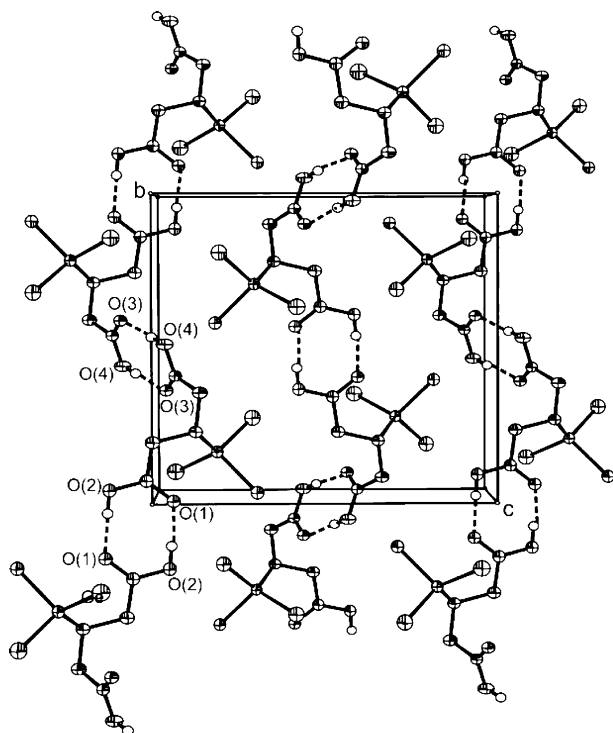|	**1**	**2**
Empirical formula	$C_5H_7Cl_3GeO_4$	$C_5H_7Cl_3GeO_4$
Formula weight	310.05	310.05
Crystal system	monoclinic	monoclinic
Space group	$P\,2_1/n$	$P\,2_1/n$
$a/$Å	6.4430(1)	6.8190(2)
$b/$Å	13.1950(2)	6.3200(1)
$c/$Å	12.7550(2)	24.1470(6)
$\beta/°$	90.844(1)	97.796(1)
$V/$Å^3	1084.25(3)	1031.02(4)
Z	4	4
θ range/°	5.43 to 30.03	3.33 to 27.46
Unique reflections	3129	2336
	$[R(\text{int}) = 0.0376]$	$[R(\text{int}) = 0.0445]$
Final $R1$, $wR2$ indices $[I > 2\sigma(I)]$	0.0274, 0.0662	0.0249, 0.0583
$R1$, $wR2$ indices (all data)	0.0292, 0.0678	0.0298, 0.0600

Table 2 Selected bond lengths/Å and bond angles/° for **1**

Ge–C(3)	1.9626(16)	C(3)–Ge–Cl(2)	115.35(5)
Ge–Cl(2)	2.1255(5)	C(3)–Ge–Cl(1)	113.32(5)
Ge–Cl(1)	2.1359(5)	Cl(2)–Ge–Cl(1)	107.15(2)
Ge–Cl(3)	2.1424(4)	C(3)–Ge–Cl(3)	112.32(5)
O(1)–C(1)	1.223(2)	Cl(2)–Ge–Cl(3)	105.65(2)
O(2)–C(1)	1.3137(19)	Cl(1)–Ge–Cl(3)	101.90(2)
O(2)–H(2)	0.88(3)	C(1)–O(2)–H(2)	110(2)
O(4)–H(4)	0.80(3)	C(5)–O(4)–H(4)	110(2)

particular interest in these structures is the effect of the Cl₃Ge subsititution on the pattern of hydrogen bonding between dicarboxylic acids. In all the four parent acids, one-dimensional supramolecular chains are formed *via* conventional "head-to-tail" acid dimers at both ends of each monomer [14].

In the structure of **1**, two carboxylic acids are positioned symmetrically with respect to the trichlorogermyl group, each carboxylic acid pairs with a single partner from another molecule to generate the conventional "head-to-tail" dimeric motif of the parent acid [15].

These strong intermolecular hydrogen bonds O–H–O result in eight membered rings (Fig. 2) that can be represented in terms of the graph set notation $R_2^2(8)$ [16, 17]. As a result, the pattern of hydrogen bonds generates a regular one-dimensional chain (Fig. 3). There are no interactions between the chains nor any involvement of the Cl₃Ge unit in hydrogen bonding, though we have observed the latter in related molecules [18].

In contrast, the asymmetric substitution in **2** (Fig. 4) results in each carboxylic acid forming hydrogen bonds with two neighboring molecules, generating sheets approximately in the *ab* direction (Figs. 3 and 4). Hydrogen bonds between O(2)···O(3) propagate in the *b* direction, while analogous O(1)···O(4) hydrogen bonds propagate along *a*. These sheets are isolated from each other by the Cl₃Ge units which form layers above and below the hydrogen bonded sheets.

The robust synthons that occur repeatedly in crystal structure are useful in crystal design. In this context, 75 common ring motifs assembled with O–H–O, N–H–O and O–H–N hydrogen bonds in the Cambridge Structural Database (CSD, October 1996, *ca.* 160000 entries) have been classified [19]. Although carboxylic acids are the second most common category of molecules archived in the CSD, the occurrence frequency for the dimer is surprisingly low at *ca.* 33%, though this is viewed as an artifact of the fact that in many carboxylic acid molecules other competing hydrogen bonding functionalities are often possible. However, when structures con-
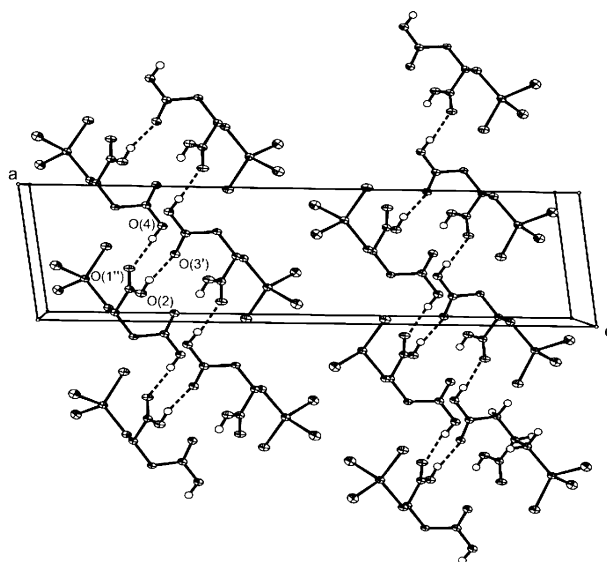

Fig. 3 The lattice structure of **2** viewed along *b*. Symmetry operations: ′1/2 − x, 1/2 + y, 1/2 − z; ″−1 + x, y, z

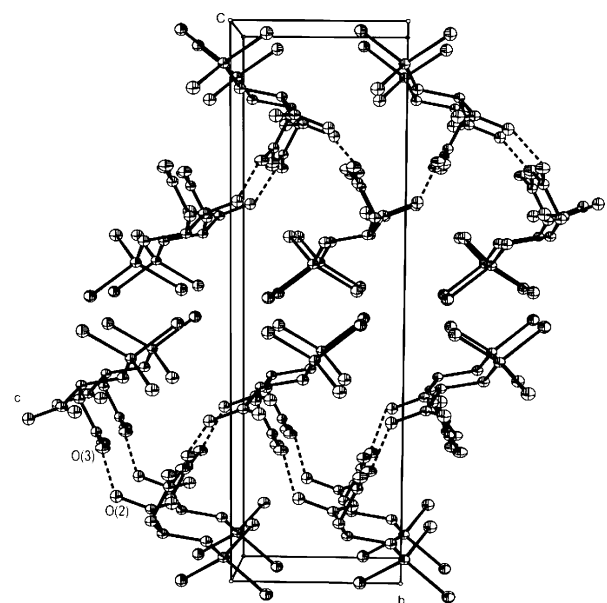**Fig. 4** The formation of hydrogen-bonded sheets in the lattice structure of **2**. Propagation along *a* involving O(1)···O(4) hydrogen bonds is obscured in this orientation

Table 3 Hydrogen bonding (Å, °) in **1**

D–H–A	D–H	H–A	D–A	<D–H–A
O(2)–H(2)–O(1′)	0.88(4)	1.74(4)	2.616(2)	177.4(9)
O(4)–H(4)–O(3″)	0.80(4)	1.85(4)	2.649(2)	180(5)

Symmetry operations: ′1 − x, −y, −z; ″−x, 1−y, −z

Table 4 Selected bond lengths/Å and bond angles/° for **2**

Ge(1)–C(1)	1.9374(19)	C(1)–Ge(1)–Cl(3)	115.61(6)
Ge(1)–Cl(3)	2.1215(5)	C(1)–Ge(1)–Cl(2)	118.81(6)
Ge(1)–Cl(2)	2.1350(5)	Cl(3)–Ge(1)–Cl(2)	106.31(2)
Ge(1)–Cl(1)	2.1523(5)	C(1)–Ge(1)–Cl(1)	105.33(6)
O(1)–C(3)	1.219(2)	Cl(3)–Ge(1)–Cl(1)	106.68(2)
O(2)–C(3)	1.318(3)	Cl(2)–Ge(1)–Cl(1)	102.70(2)
O(2)–H(2)	0.81(3)	C(3)–O(2)–H(2)	108(2)
O(4)–H(4)	0.82(4)	C(5)–O(4)–H(4)	111(2)

Table 5 Hydrogen bonding (Å, °) in **2**

D–H–A	D–H	H–A	D–A	$<D$–H–A
O(2)–H(2)–O(3$'$)	0.81(3)	1.85(3)	2.646(2)	167(3)
O(4)–H(4)–O(1$''$)	0.82(3)	1.88(4)	2.690(2)	171(4)

Symmetry operations: $'1/2 - x, 1/2 + y, 1/2 - z$; $''-1 + x, y, z$

taining only carboxylic acids as hydrogen bonding components are considered, the dimer motif has *ca.* 95% probability, dropping only slightly (to 85%) when only dicarboxylic acids are considered. The structure of **2** is neither a linear catemer nor an intramolecular S(7) motif, the usual alternatives to the dimer, and is thus an unusual variation in structural carboxylic acid chemistry. The intermolecular hydrogen bonds O–H–O in **2** result in a network of twenty two-atom rings, including four sets of hydrogen bonds in sheets. This can be represented in graph set notation as R_4^4 (22), which is rare among ring motifs of carboxylic acids. The difference in supramolecular arrangement between **1** and **2** seems to result not from any electronic or steric effects (the GeCl$_3$ unit is common to both species and adopts a similar position either side of the H-bonded chains in both cases), nor do the GeCl$_3$ units involve themselves in hydrogen bonds.

Conclusions

3-(Trichlorogermyl)pentanedioic acid **1**, 2-[(trichlorogermyl)methyl]butanedioic acid **2**, 2-(trichlorogermyl)butanedioic acid **3** and 2-methyl-3-(trichlorogermyl)butanedioic acid **4** were prepared by hydrogermylation reaction and characterized by physicochemical methods such as melting point, CHN, FTIR, multinuclear NMR (^{1}H; ^{13}C; H,H–COSY) and single crystal X-ray diffraction analyses. It was found that a hydrogermylation reaction of unsaturated dicarboxylic acids proceeds *via* 1,4 *Michael* addition to the double bond yielding a single regioselective product. Structurally, 3-(trichlorogermyl)pentanedioic acid **1** adopts a conventional head-to-tail dimerisation of carboxylic acids groups producing a regular one-dimensional chain. In contrast, 2-[(trichlorogermyl)methyl]butanedioic acid **2** forms a double-stranded chain incorporating rare 22 atom rings by virtue of the asymmetric location of the GeCl$_3$ substituent. In these structures the Cl$_3$Ge moiety acquires a passive position between

the chains without any involvement in further hydrogen bonding but keeping the chains apart.

Experimental

trans-Glutaconic acid (2-pentenedioic acid), itaconic acid (methylenebutanedioic acid), fumaric acid (2-butenedioic acid), citraconic acid (2-methyl-2-butenedioic acid) and sodium dihydrogen phosphate monohydrate (Aldrich) were used as received. Melting points were recorded on a Mitamura Riken Kogyo (MP-D) apparatus. Elemental results were obtained on Exeter analytical 440 CHNOS elemental analyzer; their results agreed favorably with the calculated values. Infrared (IR) spectra were obtained on Bio-Rad Excalibure FTIR Model 3000 MX as KBr pellets. All ^{1}H and ^{13}C NMR measurements were performed in CD$_3$OD solution on a Bruker, Avance 300 MHz digital NMR.

Crystals of **1** and **2** suitable for X-ray analysis were grown by dissolving the respective compound (0.5 g, 1.61 mmol) in (5 cm^3) acetone, to which a few drops of *n*-hexane were added. Slow evaporation of the solvent at room temperature over a period of several days yielded fine crystals which were subsequently washed with petroleum ether. Details of crystallography, geometric parameters and hydrogen bonding geometry for **1** and **2** are given in Tables 1–5. The datasets were collected on crystals of size *ca.* $0.25 \times 0.25 \times 0.25$ mm^3 at 150 K on a Nonius Kappa CCD diffractometer using graphite monochromatized Mo Kα radiation; Lp and absorption corrections (semi-empirical from equivalents) were applied. Refinement was full-matrix least squares on F^2. Hydrogen atoms were included at calculated positions, save for the acid hydrogen which was located and refined.

Software used: SHELXS 86[20], SHELXL 97 [21], ORTEX [22].

Synthesis
Compounds **1–4** were synthesized following the standard literature method [11, 23]. GeO$_2$ (5.047 mmol, 1 equiv) was added to NaH$_2$PO$_2 \cdot$ H$_2$O (10.0956 mmol, 2 equiv), 50 cm^3 HCl (37%), and 15 cm^3 distilled water in a round bottom flask. The reaction mixture was refluxed to a transparent solution. It was then cooled at 0 °C and 1 equiv of appropriate unsaturated dicarboxylic acid added, along with 30 cm^3 diethyl ether. This mixture was then stirred for 24 h at room temperature. After completion, the organic layer was separated and the product was extracted twice with 20 cm^3 ether. All organic layers were collected, dried over anhydrous MgSO$_4$, and filtered. The solvent was removed *in vacuo* to give viscous liquid which was dissolved in 3 cm^3 concentrated HCl for crystallization; white crystalline solids were isolated for all compounds **1–4**.

3-(Trichlorogermyl)pentanedioic acid (**1**, C$_5$H$_7$Cl$_3$GeO$_4$)
White crystals, 73% yield; mp = 159–162 °C; IR (KBr): $\bar{\nu} =$ 422 (Ge–Cl), 580 (Ge–C), 1701 (C=O)$_{asy}$, 1255 (C=O)$_{sym}$, $\Delta\bar{\nu} = 446$, 3300 (OH) cm^{-1}; ^{1}H NMR: $\delta = 1.45$ (m, 1H, HCGeCl$_3$), 2.83 (m, 4H, HC–(CH_2CO$_2$H)$_2$) ppm; ^{13}C NMR: $\delta = 172.5$ (C=O), 33.6 (CH$_2$), 33.0 (CH) ppm.

2-[(Trichlorogermyl)methyl]butanedioic acid
(**2**, $C_5H_7Cl_3GeO_4$)

White crystals, 74% yield; mp = 115–117°C; IR (KBr): $\bar{\nu}$ = 425 (Ge–Cl), 589 (Ge–C), 1701 (C=O)$_{asym}$, 1255 (C=O)$_{sym}$, $\Delta\bar{\nu}$ = 446, 3200 (O–H) cm^{-1}; ^{1}H NMR: δ = 1.31 (m, 1H, *H*CCO$_2$H), 2.52 (m, 2H, C*H*$_2$COOH, 3.11 (m, 2H, C*H*$_2$GeCl$_3$) ppm; ^{13}C NMR: δ = 176.0 173.9, (C=O), 36.0 (CH$_2$GeCl$_3$), 36.5 (CH$_2$), 35.8 (CH) ppm.

2-(Trichlorogermyl)butanedioic acid (**3**, $C_4H_5Cl_3GeO_4$)

White crystals, 63% yield; mp = 165–170°C; IR (KBr): $\bar{\nu}$ = 425 (Ge–Cl), 582 (Ge–C), 1725 (C=O)$_{asym}$, 1255 (C=O)$_{sym}$, $\Delta\bar{\nu}$ = 470, 3200 (O–H) cm^{-1}; ^{1}H NMR: δ = 2.16 (m, 1H, C*H*GeCl$_3$) 2.33 (m, 2H, C*H*$_2$COOH) ppm; ^{13}C NMR: δ = 174.5, 172.6 (C=O), 28.2 (CH$_2$), 30.2 (CH) ppm.

2-Methyl-3-(trichlorogermyl)butanedioic acid
(**4**, $C_5H_7Cl_3GeO_4$)

White crystals, 79% yield; mp = 140–143°C; IR (KBr): $\bar{\nu}$ = 422 (Ge–Cl), 580 (Ge–C), 1729 (C=O)$_{asym}$, 1255 (C=O)$_{sym}$, $\Delta\bar{\nu}$ = 464, 3200 (O–H) cm^{-1}; ^{1}H NMR: δ = 1.17 (d, 1H, ^3J = 6.9 Hz, *H*CGeCl$_3$), 3.16 (m, 1H, C*H*CH$_3$), 1.37 (d, 3H, ^3J = 6.9 Hz, CHC*H*$_3$) ppm; ^{13}C NMR: δ = 172.4, 169.8 (C=O), 36.0 (CH$_2$), 35.8 (CH), 18.7 (CH$_3$) ppm.

Supplementary material

Atomic coordinates, thermal parameters, bond lengths and angles for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre with CCDC Nos 293681 and 293680, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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