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Germanium carboxylates: the first X-ray diffraction study of germanium(II) dicarboxylate and germanium(IV) tetracarboxylate

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Germanium(II) dipropionate (1) has been synthesized and its crystal structure, as well as that of germanium(IV) tetrapropionate (2), has been determined. By contrast to monomeric 2 with monodentate propionate ligands, compound 1 is associated, forming a cyclotetramer $[Ge(O_2CEt)_2]_4$ (1a) via intermolecular dative $C{=}O \rightarrow Ge$ interactions. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; germanium(II); germanium(IV); carboxylates

INTRODUCTION

There is continuing interest in the synthesis and characterization of stable organic derivatives of divalent germanium and tin-heavier congeners of carbenes. Whereas the chemistry of tin(II) carboxylates is well developed, far less is known about the corresponding germanium(II) compounds. Mazières *et al.*[1] have described the physical–chemical properties and reactivity of new five- and six-membered ring heterocyclic germanium(II) carboxylates, which, on the basis of their spectroscopic data (mass, IR and ^{13}C NMR), are thought to have either dimeric or polymeric structures. Quite recently, we reported the synthesis of the first germanium(II) acetates $Ge(O_2CMe)_2$ and $(MeCO_2)GeOCH_2CH_2NMe_2$ (**3**),[2] and structural characterization of the latter by X-ray diffraction. However, no structurally characterized germanium compounds containing more than one carboxylate ligand have been reported so far.

Here, we report on the synthesis and first X-ray diffraction study of a germanium(II) carboxylate, germanium(II) propionate $Ge(O_2CEt)_2$ (**1**), which crystallizes in the tetrameric form $[Ge(O_2CEt)_2]_4$ (**1a**). For a more systematic structural investigation of this hitherto barely studied class of compounds, we have also carried out the X-ray diffraction study of a germanium(IV) carboxylate, germanium(IV) propionate $Ge(O_2CEt)_4$ (**2**), which, in contrast to tetrameric **1**, is a monomer in the solid state.

EXPERIMENTAL

General procedures

All manipulations were carried out under a purified argon atmosphere by the use of standard Schlenk and high-vacuum-line techniques. The commercially available solvents were distilled immediately prior to use. $GeCl_2$ was prepared according to the procedures described in the literature.[3] NMR spectra were recorded on a Bruker AM-360 NMR

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spectrometer at 360.134 MHz (^1H) and 90.555 MHz (^{13}C) for the samples in $CDCl_3$ and C_5D_5N. Chemical shifts are relative to $SiMe_4$. The accuracy of the coupling constant determination is ±0.1 Hz, and the accuracies of the chemical shift measurements are ±0.01 ppm for ^1H and ±0.05 ppm for ^{13}C. FTIR spectra were recorded on a Magna-750IR (Nicolet) Fourier spectrometer with a resolution of 2 cm^{-1}. The samples were prepared as Nujol mulls and CH_2Cl_2 solutions under a dry argon atmosphere.

Synthesis of Me_3GeO_2CEt

Me_3GeO_2CEt was prepared by refluxing of Me_3GeCl (13.5 g, 88.2 mmol) and NaO_2CEt (16.9 g, 176.4 mmol) in tetrahydrofuran (THF; 150 mL) followed by filtration and distillation; yield 68.7%, b.p. 142–144 °C/1 Torr, $n_D^{20} = 1.4261$. ^1H NMR (360.134 MHz, CD_3Cl): $\delta = 0.49$ (s, 9 H, Me_3Ge), 1.01 (t, 3 H, $^3J_{HH} = 7.5$ Hz, CH_3), 2.20 (q, 2 H, $^3J_{HH} = 7.5$ Hz). Elemental analysis (%). Found: C, 37.54; H, 7.21. Calc. for $C_6H_{14}GeO_2$ ($M_r = 190.76$): C, 37.78; H, 7.40.

Synthesis of $Ge(O_2CEt)_2$ (1)

A solution of Me_3GeO_2CEt (6.28 g, 32.9 mmol) in THF (20 mL) was added at room temperature to a stirred solution of $GeCl_2{\cdot}D$ (D = dioxane; 3.82 g, 16.5 mmol) in THF (30 mL). After 30 min the mixture was filtered. The solvent was removed *in vacuo* and the residue was evaporated at 50–60 °C/1 Torr; the volatiles condensed in a liquid-nitrogen-cooled trap. The yield of white solid is 3.43 g (95.4%). The resulting product crystallized from THF at −12 °C, giving **1a** as white crystals; m.p. 66.5–67.5 °C (in sealed capillary). ^1H NMR (360.134 MHz, C_5D_5N): $\delta = 1.06$ (t, 24 H, $^3J_{HH} = 7.5$ Hz), 2.33 (q, 16 H, $^3J_{HH} = 7.5$ Hz). ^{13}C NMR (90.555 MHz, C_5D_5N): $\delta = 10.06$ (br, $\Delta\nu_{1/2} = 4.4$ Hz, Me), 29.67 (CH_2), 180.09 (C=O). Elemental analysis (%). Found: C, 32.77; H, 4.47. Calc. for $C_{24}H_{40}Ge_4O_{16}$($M_r = 874.92$): C, 32.95; H, 4.61.

Synthesis of $Ge(O_2CEt)_4$ (2)

A solution of $GeBr_4$ (4.68 g, 11.9 mmol) in C_6H_{14} (10 mL) was added at room temperature to a stirred solution of $Bu_2Sn(OOCEt)_2$ (9.03 g, 23.8 mmol) in C_6H_{14} (10 mL). The mixture was cold to 0 °C. The white crystals were filtered, washed by C_6H_{14}, and dried *in vacuo*. Yield (79.8%), m.p. 90–91 °C (in sealed capillary), in accordance with the literature data.[4] ^1H NMR (360.134 MHz, $CDCl_3$): δ 1.08 (t, 12 H, $^3J_{HH} = 7.5$ Hz), 2.40 (q, 8 H $^3J_{HH} = 7.5$ Hz). ^{13}C NMR (90.555 MHz, $CDCl_3$): $\delta = 8.99$(CH_3), 29.99 (CH_2), 176.99 (C=O). Elemental analysis (%). Found: C, 39.67; H, 5.43. Calc. for $C_{12}H_{20}GeO_8$($M_r = 364.87$): C, 39.50; H, 5.52.

Crystal structure determinations

Data were collected at 120 K on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector and corrected for Lorentz and polarization effects and for absorption.[5] For details see Table 1. The structures were solved by direct methods and refined by a full-matrix least-squares method, on F^2, with anisotropic displacement parameters for non-hydrogen atoms. The absolute structure of **2** was confirmed by the value of the Flack parameter of 0.056(12). The hydrogen atoms in **1a** were placed in calculated positions and refined in the riding model with fixed thermal parameters. The hydrogen atoms in **2** were located from the difference Fourier syntheses and refined isotropically. All calculations were carried out using the SHELXTL PLUS program (PC Version 5.0).[6] CCDC deposition numbers: 234703 (**1a**) and 234704 (**2**).

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

	1a	**2**
Empirical formula	$C_{24}H_{40}O_{16}Ge_4$	$C_{12}H_{20}O_8Ge$
Formula weight	874.92	364.87
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I\bar{4}$
a (Å)	15.7289(8)	11.1284(10)
c (Å)	13.2671(10)	6.4491(8)
V(Å^3)	3282.3(3)	798.66(14)
Z	4	2
d_c(g cm^{-3})	1.771	1.517
μ(mm^{-1})	3.698	1.951
θ range (°)	2.0 to 28.0	2.6 to 29.9
Measured/ independent reflections/R_{int}	9630/1968/0.037	4675/1153/0.041
reflns with $I > 2\sigma(I)$	1479	1149
R_1; wR_2($I > 2\sigma(I)$)	0.032; 0.065	0.024; 0.054
R_1; wR_2 (all data)	0.048; 0.068	0.024; 0.054

RESULTS AND DISCUSSION

The compound $Ge(O_2CEt)_2$ **1** is formed easily in 95% yield by the exchange reaction of $GeCl_2{\cdot}D$ with two equivalents of Me_3GeO_2CEt in THF at room temperature:

$$GeCl_2{\cdot}D + 2Me_3GeO_2CEt \rightarrow Ge(O_2CEt)_2 + 2Me_3GeCl + D \quad (1)$$

Compound **1** is a white crystalline substance that is very sensitive to traces of oxygen and moisture. It is moderately soluble in THF and pyridine, slightly soluble in benzene, and insoluble in hexane.

Single crystals of **1** and **2** suitable for X-ray crystallography were obtained from THF solutions. Interestingly, compound **1** crystallizes in the tetrameric form $[Ge(O_2CEt)_2]_4$ (**1a**). The IR spectrum of **1** in Nujol has two ν(C=O) bands at 1640 cm^{-1} (free C=O group) and 1549 cm^{-1} (coordinated C=O group), which is consistent with the associated tetrameric structure

1a. A similar low-frequency shift of about 100 cm^{-1} upon association was also found by Mazières *et al.* in the IR spectra of solid associated five-membered ring heterocyclic germylenes.[1] The low-frequency band at 1544 cm^{-1} remains in CH_2Cl_2 solution of **1**, and its relative intensity decreases upon dilution. This observation apparently proves the keeping of the association of **1** in neutral solvents.

The molecular structures of **1a** and **2**, along with the atomic numbering schemes and selected bond lengths and angles, are shown in Figs 1 and 2.

Complex **1a** crystallizes in the tetragonal space group $I4_1/a$, and occupies a special position on the four fold inversion axis. In **1a**, a germanium atom is attached to three oxygen atoms from three different propionate ligands. Two of the three propionate ligands are intermolecularly bridged to germanium atoms via dative C=O → Ge interactions forming a cyclotetramer, and one propionate ligand is terminal. The coordination geometry about germanium is derived from a distorted tetrahedron (Fig 1) with a stereochemically active lone pair, as is commonly observed for compounds of the form $[E^{14(II)}X_3]$ (E^{14} = Ge, Sn, Pb).[7] The terminal Ge–O3 bond length in **1a** (1.899(2) Å) is shorter, but the bridging Ge–O1 (2.021(2) Å) and Ge–O2^{i} (1.977(2) Å) bond lengths are longer than the Ge–O(acyloxy) bond length in **3** (1.938(1) Å). Similar Ge–O bond lengths are present in the dimers $[t\text{-}BuOGeOSiPh_3]_2$ (Ge–O(terminal) 1.814(6), Ge–μ^2-O 1.966(6), 1.967(6) Å)[8] and $[Ge(OAr^*)_2]_2$ (Ar^* = 2,6-i-$Pr_2C_6H_3$ (Ge–O(terminal) 1.823(2) and 1.824(2) Å, Ge–μ^2-O 1.981(2), 2.012(2) Å and 1.988(2), 2.008(2) Å) or 2,4,6-$Me_3C_6H_2$ (Ge–O(terminal) 1.828(3) and 1.822(3) Å, Ge–μ^2-O 1.984(3), 1.984(3) Å and 1.981(3), 1.987(3) Å))[9] and in the binuclear germanium calix[4]arene [t-Bu-calix]Ge_2 (Ge–O(terminal) 1.844(6) Å, Ge–μ^2-O 1.991(6), 1.997(6) Å).[10] The O–Ge–O bond angles are close to those observed in previously studied three-oxygen-coordinate germanium(II) compounds.[8–13] Oligomeric polynuclear complexes with bridging carboxylate ligands are typical for transition metals, but compound **1a** is the first example of such a complex among the non-transition elements.

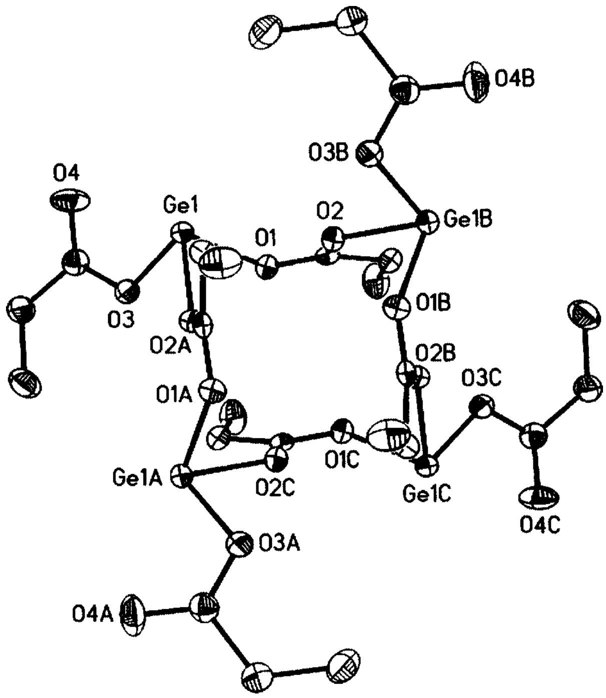

Figure 1. Molecular structure of **1a** with 50% probability ellipsoids and with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ge–O1 2.021(2), Ge–O2^{i} 1.977(2), Ge–O3 1.899(2), O1–Ge–O2^{i} 87.25(8), O1–Ge–O3 87.32(9), O2^{i}–Ge–O3 83.97(9). Symmetry operation i: $11/4 - y$, $1/4 + x$, $1/4 - z$.

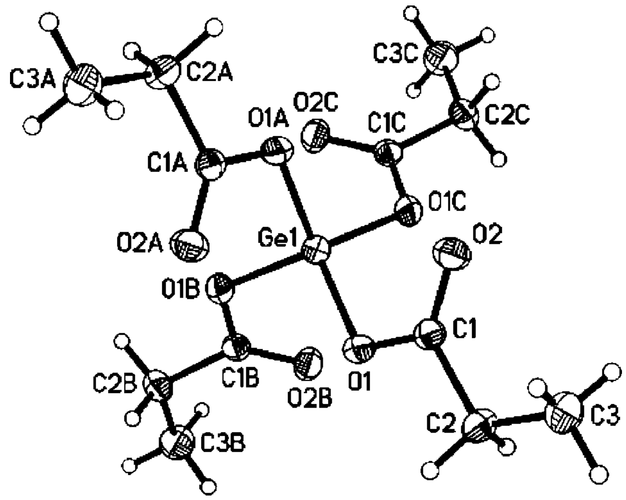

Figure 2. Molecular structure of **2** with 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Ge–O1 1.775(1), O1–Ge–O1^{i} 122.69(9), O1–Ge–O1^{ii} 103.29(4). Symmetry operation i: $-x$, $-y$, z; ii: y, $-x$, $-z$.

Like for **3** (2.753(1) Å),[2] the propionate ligands in **1a** do not exhibit any intra-chelate Ge–O interactions [Ge···O2 2.855(2) Å, G···O4 2.932(2) Å and Ge···O1^{i} 4.086(2) Å]. The shortest Ge···O distance between tetramers is Ge···O4 ($0.25 + y$, $1.25 - x$, $0.25 + z$) of 2.813(2) Å, altering the distorted tetrahedral configuration of germanium to distorted trigonal bipyramidal with a lone pair in the equatorial position.

A theoretical density functional theory (DFT) study (PBE/TZ2P) showed that the $Ge(O_2CEt)_2$ in the gas phase should exist as a monomer with the O_2CEt groups coordinated to the germanium atom in a chelate fashion. Formation of cyclotetrameric **1a** from the four monomer units gains −7.7 kcal mol^{-1} with respect to one subunit. In the optimized gas-phase structure of **1a**, the difference between Ge–O1 and Ge–O2^{i} bond lengths was found to be 0.127 Å (cf. 0.044 Å in X-ray structure). Crystal packing effects can cause such geometric changes.

Complex **2** crystallizes in the tetragonal space group $I\bar{4}$, and, similar to **1a**, occupies a special position on the four fold inversion axis. However, in contrast to **1a**, compound **2** is a monomer with four monodentate propionate ligands. The germanium atom in **2** adopts a distorted tetrahedral geometry (Fig. 2). As might be expected, much shorter Ge–O bond lengths than those in **1a** are found in **2** (1.775(1) Å) due to the smaller radius of Ge^{IV} relative to Ge^{II} and the covalent character of all Ge^{IV}–O bonds. It is interesting to note that the intra-chelate Ge···O distances in **2** [Ge···O2 2.769(1) Å] are slightly longer than the intra-chelate Ge···O distance in **3**, but considerably shorter than those in **1a**.

The investigations of other germanium carboxylates are in progress.

SUPPLEMENTARY MATERIALS

Results of DFT calculations.

Acknowledgements

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