

# Polyol Metal Complexes. Part 55<sup>1)</sup> Germanes with Alkylenedioxy Substituents

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*Dedicated to Professor Wolfgang Beck on the Occasion of his 75<sup>th</sup> Birthday*

**Abstract.** Within this work five novel germanes with alkylenedioxy substituents derived from 1,2-diols have been synthesized and structurally characterized. Various coordination patterns from tetra- to hexacoordination were determined. Both open-chain and cyclic 1,2-diols such as 1,2-ethandiol (Ethd), 1,1'-bicyclohexyl-1,1'-diol (Bhxd), *cis*-oxolane-3,4-diol (AnEryt) and *cis*-1,2-cyclopentandiol (*cis*-1,2-Cptd) were used. Tetracoordination of the germanium atom in the crystalline state appears to be restricted to sterically demanding substituents.

In general, the tendency of germanium to extend its coordination sphere to build penta- or hexacoordinate compounds is demonstrated. It is also shown that germanium is able to compensate a lack of substituents by the formation of dimeric structures.

**Keywords:** Germanium; Alkylenedioxy substituents; Crystal structure

## Introduction

Only about two dozen germanium–oxygen compounds with 1,2-diols have been structurally characterized to date. A tendency of germanium to extend its coordination sphere has been confirmed. In alkaline aqueous solution, for example, the pentacoordinate complex  $\text{Li}[\text{Ge}(\text{AnErytH}_{-2})_2(\text{OH})]\cdot\text{H}_2\text{O}$  was obtained with the furanose-related oxolanediolato ligand [1]. The more complex ligand  $\beta$ -cyclodextrin was used to synthesize the hexacoordinate compound  $[\{\text{Li}(\text{H}_2\text{O})_4\}_3\{\Lambda\text{-Ge}(\beta\text{-CDH}_{-2})_3\}]\text{H}_{-1}\cdot 24 \text{H}_2\text{O}\cdot 3 \text{EtOH}$  from strongly alkaline aqueous solution [2]. Thus, the number of germanes with a chelating oxygen coordination environment characterized by X-ray diffraction is added up to just one [3]. In contrast to diolato germanate chemistry, there is only little knowledge of the electroneutral parent compounds, the diol-derived germanes.

Within this work, 1,2-diols related to carbohydrates were used. Keeping in mind the close relationship between silicon and germanium, this study was designed to contribute

to a better understanding of the carbohydrate coordination chemistry of both elements. Due to their size, germanium atoms may be particularly capable of stabilizing conceivable higher-coordinated intermediates which probably could not be intercepted in the case of silicon. The coordination chemistry of germanium thus appears to be significant for an understanding of possible intermediates in the course of silica biomineralisation.

There is, therefore a backlog in demand for collecting basic information about the reaction behavior of germanium towards diol functions and making use of the results to deduce basic rules. Due to germanium's tetravalency, spiro-germanes of the type  $\text{Ge}(\text{DiolH}_{-2})_2$  should be key compounds in this chemistry. All the more astonishing, then, is the fact that no structurally characterized tetracoordinate oxygen spiro-germane has been determined to date.

## Experimental Section

### Physical measurements

<sup>1</sup>H NMR spectra were measured with a Jeol spectrometer at 400 MHz, <sup>13</sup>C NMR spectra were measured with a Jeol spectrometer at 70 MHz and a Jeol spectrometer at 100 MHz. MS were carried out at a MS 700 spectrometer from Jeol.

### Crystallography

The intensity data of the complexes were collected using a Stoe IPDS (2 and 5) or a Kappa CCD (1, 3 and 4) diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) at 200 K. The structures were solved using the programs SHELXS-97 [4] (1, 2, 3), SIR97 [5] (4, 5), and

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**Table 1** Crystallographic data and details of the structure determination of **1**, **2**, **3**, **4** and **5**

compound	1	2	3	4	5
empirical formula	C <sub>96</sub> H <sub>160</sub> Ge <sub>4</sub> O <sub>16</sub>	C <sub>20</sub> H <sub>32</sub> Ge <sub>2</sub> O <sub>8</sub>	C <sub>9</sub> H <sub>16</sub> GeO <sub>7</sub>	C <sub>8</sub> H <sub>20</sub> GeO <sub>8</sub>	C <sub>4</sub> C <sub>12</sub> H <sub>10</sub> O <sub>4</sub> Ge
<i>M<sub>r</sub></i> /g mol <sup>-1</sup>	1860.73	545.68	308.83	316.89	265.64
crystal system	triclinic	monoclinic	triclinic	triclinic	trigonal
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 3 <sub>2</sub> 21
<i>a</i> /Å	11.1879(2)	10.188(2)	5.7318(3)	4.9200(3)	8.7997(8)
<i>b</i> /Å	11.2119(2)	10.804(2)	9.6753(5)	7.2620(4)	
<i>c</i> /Å	18.9091(4)	9.5510(19)	10.5215(6)	8.6030(5)	9.8122(11)
$\alpha$ /°	103.0354(10)	90	73.873(2)	71.866(3)	
$\beta$ /°	94.0217(9)	93.98(3)	88.491(2)	85.030(3)	
$\gamma$ /°	90.0585(9)	90	84.679(3)	84.270(4)	
<i>V</i> /Å <sup>3</sup>	2304.75(8)	1048.8(4)	558.11(5)	290.15(3)	658.01(11)
<i>Z</i>	1	2	2	1	3
$\rho$ /g cm <sup>-3</sup>	1.34065(5)	1.7280(7)	1.83774(16)	1.80183(19)	2.0111(3)
$\mu$ /mm <sup>-1</sup>	1.356	2.912	2.767	2.669	0.71073
crystal size/mm	0.20×0.14×0.06	0.18×0.18×0.13	0.32×0.10×0.06	0.14×0.04×0.03	0.39×0.29×0.17
temperature/K	200(2)	200(2)	200(2)	200(2)	200(2)
diffractometer	KappaCCD	Stoe IPDS	KappaCCD	KappaCCD	Stoe IPDS
radiation	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$
anode	rotating anode	fine-focus sealed tube	rotating anode	rotating anode	fine-focus sealed tube
rated input/kW	3.025	2.75	4.125	4.050	2.75
$\theta$ range/°	3.20–25.00	2.00–26.03	3.57–27.37	3.24–27.50	2.67–27.92
reflections	9580	3652	12085	12790	5000
absorption correction	multiscan	numerical	numerical	numerical	numerical
transmission factor range	–	–	–	0.7876–0.9366	0.3532–0.5666
refls. measured	15265	7075	8609	4802	5644
observed reflections	8073	1903	2497	1301	1056
<i>R</i> <sub>int</sub>	0.0393	0.0840	0.0629	0.0742	0.0330
mean $\sigma(I)/I$	0.0567	0.1007	0.0633	0.0610	0.0182
reflections in refinement	6413	1201	2236	1274	1032
<i>x</i> , <i>y</i> (weighting scheme)	0.0761, 5.9672	0.0277, 0	0.0562, 11.5622	0, 0.2669	0.0275, 0
refinement	a)	a)	a)	a)	a)
extinction parameter	–	–	0.030(7)	–	–
parameter	523	136	158	81	71
restraints	0	0	0	0	0
<i>R</i> ( <i>F</i> <sub>obs</sub> )	0.0648	0.0353	0.0836	0.0339	0.0143
<i>R</i> <sub>w</sub> ( <i>F</i> <sup>2</sup> )	0.1680	0.0718	0.2411	0.0723	0.0381
<i>S</i>	1.069	0.798	1.211	1.083	1.085
shift/error <sub>max</sub>	0.001	0.001	3.067	0.001	0
max electron density/e Å <sup>-3</sup>	2.365 <sup>b)</sup>	0.564	3.171 <sup>c)</sup>	0.451	0.246
min electron density/e Å <sup>-3</sup>	–0.853	–0.562	–0.823	–1.269	–0.414

a) carbon-bonded hydrogen atoms in the ideal position riding on their parent atoms b) max remaining electron density at O18 (distance 1.380 Å) c) max remaining electron density at O32 (distance 1.234 Å)

SHELXL-97 [6]. The molecular diagrams were prepared by using ORTEP III [7].

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre: 635635 (**1**), 635636 (**2**), 635637 (**3**), 635638 (**4**), and 635639 (**5**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: international code+(1223)336-0333; e-mail for inquiry: file-serv@ccdc.cam.ac.uk).

### Preparation of Ge(BhxdH<sub>-2</sub>)<sub>2</sub> (**1**)

1,1'-Bicyclohexyl-1,1'-diol (0.42 g, 2.1 mmol) was dissolved in trichloromethane (2 mL) and germaniumtetrachloride (0.12 mL, 0.8 mmol) was added dropwise. The solution was heated under reflux, pyridine (0.32 mL, 4.0 mmol) in trichloromethane (1 mL) was added and the reaction mixture was refluxed for another 3 hours. After cooling to room temperature a white precipitate formed, the solvent was removed under vacuum, the pyridiniumhydrochloride was sublimated over a nitrogen cryo trap. The product was recrystallized from trichloromethane and colorless crystals were obtained; yield: <1 % [8].

<sup>1</sup>H NMR (399.8 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 0.98–1.20 (m, 4H; C4H), 1.20–1.46 (m, 8H; C2H, C6H), 1.46–1.92 (m, 28H; C2H, C3H, C4H, C5H, C6H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 22.02 (8 C; C3, C5), 25.94 (4 C; C4), 32.09 (8 C; C2, C6), 81.12 (4 C; C1) ppm.

### Preparation of {Ge(*cis*-1,2-CptdH<sub>-2</sub>)<sub>2</sub>}<sub>2</sub> (**2**)

A solution of *cis*-1,2-cyclopentanediol (0.82 g, 8.0 mmol) in 20 mL *p*-xylene was heated under reflux. Tetramethoxygermane (0.60 mL, 4.0 mmol) was added dropwise through a dropping funnel. A colorless precipitate formed within a few minutes and the mixture was refluxed for another 3 hours. The reaction solution was cooled to room temperature and colorless crystals formed within one hour; yield: 100 %.

<sup>1</sup>H NMR (400.2 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 1.22 (1 H; H5), 1.66 (2 H; H1, H4), 1.81, 1.92 (3 H; H1, H4, H5), 4.40 (2 H; H2, H3) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  = 21.36 (4 C; C5), 34.11 (8 C; C1, C4), 73.57 (8 C; C2, C3) ppm. MS (DEI<sup>+</sup>): *m/z* (%) = 274 (5) [M<sup>+</sup>/2], 174 (100) [GeO<sub>2</sub>C<sub>5</sub>H<sub>8</sub><sup>+</sup>], 145 (55) [GeO<sub>2</sub>C<sub>3</sub>H<sub>3</sub><sup>+</sup>], 117 (15) [GeOC<sub>2</sub>H<sub>4</sub><sup>+</sup>], 91 (22), 60 (25).

### Preparation of Ge(OCH<sub>3</sub>)(AnErytH<sub>-2</sub>)(AnErytH<sub>-1</sub>) (**3**)

*Cis*-oxolane-3,4-diol (0.83 g, 8.0 mmol) was suspended in 30 mL *p*-xylene and heated under reflux. Tetramethoxygermane (0.60 mL,

4.0 mmol) was added through a dropping funnel to the solution. A colorless precipitate formed immediately and the mixture was refluxed for another 3 hours. After the solvent was removed under vacuum, the colorless residue was recrystallized from methanol. Colorless crystals grew at 4 °C within 14 days; yield: <1 %.

$^{13}\text{C}\{^1\text{H}\}$  NMR (67.9 MHz,  $\text{CD}_3\text{OD}$ , 25 °C):  $\delta$  = 47.71 (1 C;  $\text{OCH}_3$ ), 71.74 (2 C; C2, C3), 74.06 (2 C; C1, C4) ppm.

### Preparation of $\text{Ge}(\text{EthdH}_{-2})_2(\text{Ethd})_2$ (4)

Tetramethoxygermane (1.00 mL, 6.7 mmol) was dissolved in 30 mL 1,2-ethanediol and the colorless solution was refluxed for 3 hours. After cooling the solution to room temperature, colorless needles formed within one day; yield: 70 %.

$^1\text{H}$  NMR (399.8 MHz,  $\text{CD}_3\text{OD}$ , 25 °C):  $\delta$  = 3.34 (8 H; H3a, H3b, H4a, H4b), 3.59 (8 H; H1a, H1b, H2a, H2b) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 25 °C):  $\delta$  = 63.00 (2 C; C1, C2) ppm. MS (DEI $^+$ ):  $m/z$  (%) = 194 [ $\text{M}^+ - \text{C}_4\text{H}_{10}\text{O}_4$ ], 134 (85) [ $\text{M}^+ - \text{C}_6\text{H}_{14}\text{O}_6$ ], 104 (100) [ $\text{GeOCH}_3^+$ ].

### Preparation of $\text{Ge}(\text{EthdH}_{-1})_2\text{Cl}_2$ (5)

Germaniumtetrachloride (0.16 mL, 1.00 mmol) and 1,2-ethanediol (0.11 mL, 2.00 mmol) were dissolved in 5 mL toluene and the colorless solution was refluxed for 4 hours. After cooling the solution to room temperature colorless crystals formed within a few hours; yield: <1 %.

$^1\text{H}$  NMR (399.8 MHz,  $\text{CD}_3\text{OD}$ , 25 °C):  $\delta$  = 4.96 (s, 4 H) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 25 °C):  $\delta$  = 63.02 (2 C) ppm.

## Results and Discussion

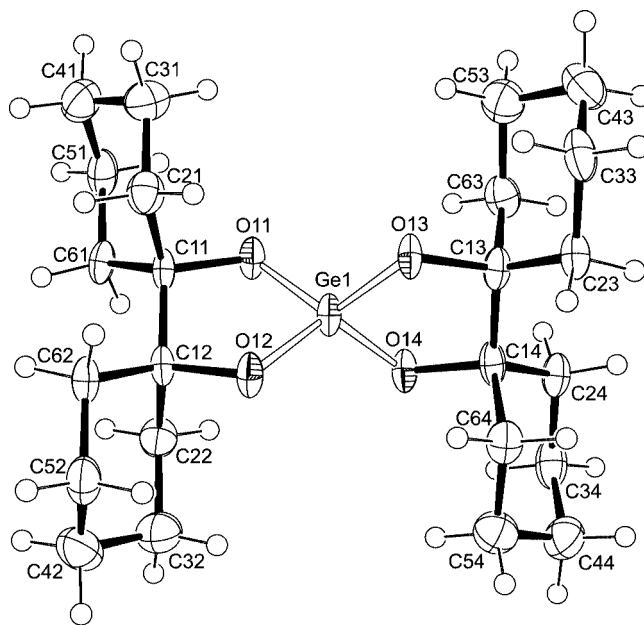
### Tetracoordination: $\text{Ge}(\text{BhxdH}_{-2})_2$

Though there is no structurally characterized tetracoordinate germanium-acid spiro ester, a compound of this type was claimed by Müller and Heinrich in 1962. The diol component was the sterically demanding 1,1'-bicyclohexyl-1,1'-diol [8].

We now succeeded in the structure determination of this compound. According to the authors, the estimated spiro-germane  $\text{Ge}(\text{BhxdH}_{-2})_2$  (1) was obtained.

The Ge-O distances of the colorless crystals range at about 1.75 Å, a selection of the most important bond lengths and angles is listed in the figure caption. Figure 1 shows one of the symmetrically independent molecules of the unit cell. Sterically exigent diols force germanium to participate in a strongly distorted  $\text{GeO}_4$ -tetrahedron. The  $^{13}\text{C}$  NMR spectrum of the reaction solution shows a coordination induced shift ( $\Delta\delta$ ) for the oxygen-binding carbon atoms ( $\text{C}1n$  5.3 ppm cf.;  $\text{C}2n/\text{C}6n$  1.3 ppm;  $\text{C}4n$  0.0 ppm;  $\text{C}3n/\text{C}5n$  0.3 ppm), whereas the downfield shift of the signals is most developed for the coordinating carbon atoms  $\text{C}1n$ .

In the next step, as a further attempt to contribute to carbohydrate-germanium chemistry, ligands that more



**Figure 1** ORTEP diagram of one of the symmetrically independent molecules of  $\text{Ge}(\text{BhxdH}_{-2})_2$  (1). Displacement ellipsoids are drawn at the 50 % probability level.

Selected bond distances in Å: Ge1-O11 1.749(3), Ge1-O12 1.749(4), Ge1-O13 1.751(3), Ge1-O14 1.749(3) and angles in °: O11-Ge1-O12 96.43(16), O11-Ge1-O13 121.21(16), O11-Ge1-O14 112.21(16), O12-Ge1-O13 111.72(16), O12-Ge1-O14 120.73(16), O13-Ge1-O14 96.35(16).

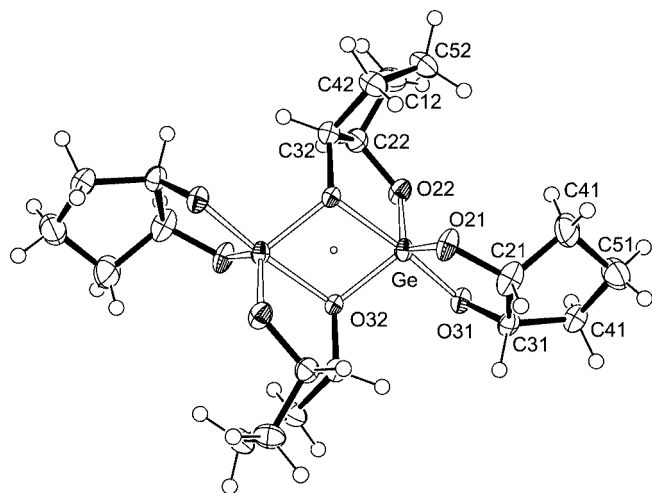
closely resemble the furanose or pyranose binding capabilities were introduced.

Using cyclic 1,2-diols like *cis*-1,2-cyclopentanediol or *cis*-oxolane-3,4-diol, two different coordination patterns were determined by X-ray diffraction.

### Pentacoordination: $\{\text{Ge}(\text{cis-1,2-CptdH}_{-2})_2\}_2$

In contrast to 1, formed with a sterically demanding diol, *cis*-1,2-cyclopentanediol resembles more closely the core of cyclic carbohydrates.  $\{\text{Ge}(\text{cis-1,2-CptdH}_{-2})_2\}_2$  (2) was formed by the transesterification of tetramethoxygermane in *p*-xylene as the solvent in a quantitative yield. The structure determination resulted in a dimeric spiro-germane. Both central atoms are surrounded by five oxygen atoms. The environment of the central atoms is close to a trigonal bipyramid. The Ge-O distances evident in the new bonds that are formed on dimerization, are longer than the average ones, but the longest distance lies between Ge and  $\text{O}32^i$  belonging to the same monomeric part. Thus, the dimeric structure appears to be a stabilized transition state of dimerization towards the monomeric molecule. Attempts to grow crystals of the monomer using the methods applied to the silicon analog failed.

The noted silicon analogs  $\{\text{Si}(\text{AnErytH}_{-2})_2\}_2$  and  $\{\text{Si}(\text{cis-1,2-CptdH}_{-2})_2\}_2$  behave in a different way. Both dimeric and monomeric polymorphs are accessed by crystallisation under various conditions [9]. Consequently, the tetracoordinate monomers are present at the smaller silicon



**Figure 2** ORTEP diagram of the  $C_i$  symmetric molecule  $\{\text{Ge}(\text{cis-1,2-CptdH}_{-2})\}_2$  (**2**). Displacement ellipsoids are drawn at the 50% probability level. The inversion center is indicated by a small circuit.

Selected bond distances in Å: Ge-O21 1.764(3), Ge-O22 1.757(2), Ge-O31 1.782(3), Ge-O32 1.844(3), Ge-O32<sup>i</sup> 2.037(2) and angles in °: O21-Ge-O31 93.66(14), O21-Ge-O32 115.90(15), O21-Ge-O22<sup>i</sup> 162.52(15), O21-Ge-O32<sup>i</sup> 87.05(13), O31-Ge-O32 99.01(12), O31-Ge-O22<sup>i</sup> 98.87(14), O31-Ge-O32<sup>i</sup> 174.96(14), O32-Ge-O22<sup>i</sup> 113.04(14), O32-Ge-O32<sup>i</sup> 76.23(11), O22<sup>i</sup>-Ge-O32<sup>i</sup> 84.67(13). <sup>i</sup> -x, -y+1, -z.

atom, whereas germanium displays a distinctive tendency towards higher coordinated compounds. Attempts to synthesize the germanium analogue using several methods failed and yielded the monomeric complex **3**.

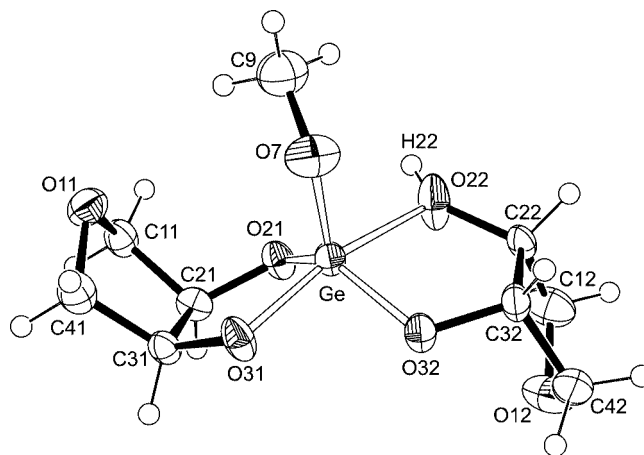
The first neutral germane of this type was synthesized by Mehrotra et al. and the crystals of  $\{\text{Ge}(\text{EthdH}_{-2})\}_2$  were obtained by dismutation of  $[(\text{O}^i\text{Pr})_2\text{Ge}(\text{EthdH}_{-2})]$  [**3**]. Since a dismutation-type reaction that loses half of the germanium is prohibited in our procedure, the class of spirogermanes now is accessible in a 100%-yield reaction.

### Pentacoordination:

#### $\text{Ge}(\text{OCH}_3)(\text{AnErytH}_{-2})(\text{AnErytH}_{-1})$

*Cis*-oxolane-3,4-diol exhibits a furanose's core. Thus taking a further step towards carbohydrate chemistry, it is particularly interesting that germanium forms a complex totally different from those expected from similar reactions with silicon. Whereas silicon results in the dimeric compound  $\{\text{Si}(\text{AnErytH}_{-2})\}_2$  [**9**] mentioned above, the transesterification of tetramethoxygermane with *cis*-oxolane-3,4-diol leads to the pentacoordinated monomer  $\text{Ge}(\text{OCH}_3)(\text{AnErytH}_{-2})(\text{AnErytH}_{-1})$  (**3**). The methoxido ligand occupies the apical position of a square pyramid. Despite of the higher coordination number, the complex is uncharged, this unusual formal chargeback is carried out intramolecularly. **3** has a protonated oxygen atom in one of the five membered chelating rings.

Although the proton H22 of the pentacoordinated complex **3** is stabilized by the formation of hydrogen bonds to



**Figure 3** ORTEP diagram of  $\text{Ge}(\text{OCH}_3)(\text{AnErytH}_{-2})(\text{AnErytH}_{-1})$  (**3**). Displacement ellipsoids are drawn at the 50% probability level. Crystal defects result in high electron density max data.

Selected bond distances in Å: Ge-O7 1.761(8), Ge-O21 1.764(7), Ge-O22 2.023(8), Ge-O31 1.836(7), Ge-O32 1.774(8) and angles in °: O7-Ge-O21 117.2(3), O7-Ge-O22 92.9(4), O7-Ge-O31 101.5(3), O7-Ge-O32 110.9(3), O21-Ge-O22 84.6(3), O21-Ge-O31 89.7(3), O21-Ge-O32 130.7(3), O22-Ge-O31 165.5(3), O22-Ge-O32 82.9(3), O31-Ge-O32 90.9(3).

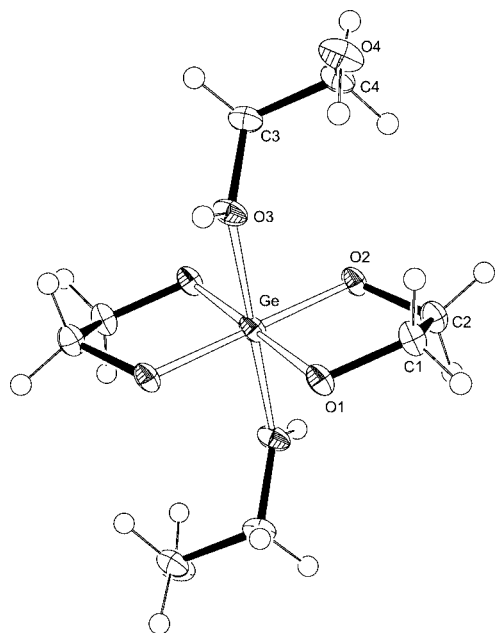
the oxygen atom O31 belonging to the adjacent complex, the structural motif of a partially un-deprotonated *cis*-oxolane-3,4-diol ligand is unique. Normally, the protonation of the coordinating oxygen atom is the first step towards the hydrolysis of the compound. This possible decomposition intermediate product was isolated and structurally characterized. In terms of proton balance, **3** resembles germanic acid which is equivalent to the protonation state of germanium under physiological conditions. Species such as **3** appear to be more representative of physiologically significant forms of silicon and germanium than the silicates and germanates described in previous works.

### Hexacoordination: $\text{Ge}(\text{EthdH}_{-2})_2(\text{Ethd})_2$

Changing from sterically demanding to unstrained ligands, the coordination pattern of protonated oxygen ligands recurs. We were able to synthesize the hexacoordinated complex **4** by transesterification of tetramethoxygermane using 1,2-ethanediol as ligand and solvent in the absence of added base. Colorless needles crystallized within a few hours after cooling the reaction solution to room temperature.

The structure determination revealed the hexacoordinated germanium compound  $\text{Ge}(\text{EthdH}_{-2})_2(\text{Ethd})_2$  (**4**) with two chelating 1,2-ethanediolato ligands in the equatorial position and two 1,2-ethanediol molecules coordinated terminally to the germanium atom in the axial positions. The structure of the complex is almost octahedral. As well as in this case, the coordination of two un-deprotonated ethanediol molecules leads to the formation of a neutral germanium compound. As expected, there is an obvious difference between the Ge-O bond lengths, which results in an axial elongation of the  $\text{GeO}_6$ -octahedron.





**Figure 4** ORTEP diagram of  $\text{Ge}(\text{EthdH}_{-2})_2(\text{Ethd})_2$  (**4**). Displacement ellipsoids are drawn at the 50% probability level.

Selected bond distances in Å: Ge-O1 1.849(2), Ge-O2 1.8159(17), Ge-O3 2.0248(17) and angles in °: O1-Ge-O2 90.07(8), O1-Ge-O3 89.16(8), O1-Ge-O1<sup>i</sup> 180.00, O1-Ge-O2<sup>i</sup> 89.93(8), O1-Ge-O3<sup>i</sup> 90.84(8), O2-Ge-O3 91.15(7), O2-Ge-O2<sup>i</sup> 180.00, O2-Ge-O3<sup>i</sup> 88.85(7), O3-Ge-O1<sup>i</sup> 90.84(8), O3-Ge-O3<sup>i</sup> 180.00. <sup>i</sup> -x, -y, -z.

### Hexacoordination: $\text{Ge}(\text{EthdH}_{-1})_2\text{Cl}_2$

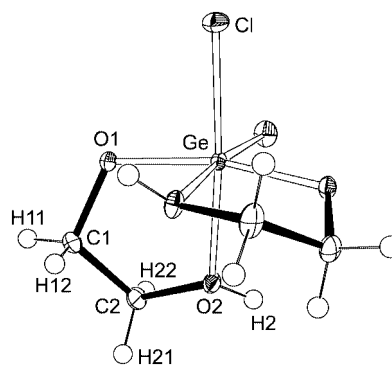
The synthesis of  $\text{Ge}(\text{EthdH}_{-1})_2\text{Cl}_2$  (**5**) leaves the 1,2-ethanediol partly un-deprotonated. Refluxing germaniumtetrachloride in 1,2-ethanediol does not result in a complete substitution of all chlorine atoms by oxygen ligands as in **4**.

While **4** shows two 1,2-ethanediol ligands in the axial position of the octahedron which are  $\kappa^1$ -binding to the germanium atom, the formal chargeback in **5** is carried out by the chelating ethanedioate(1-) ligands. The geometry of the structure, again, is nearly octahedral: the two chlorido ligands occupy one axial and one equatorial position as is shown in Figure 5. As in structure **4**, the bond distances between the central atom and the diolato, respectively, the diol function range at about 0.18 Å. The longest bonds at 2.22 Å arise between the germanium and the chlorine atoms. Again it was shown that with germanium this type of complex is not an exception, but the absence of added base in an adequate solvent leads to the formation of protonated diolato ligands.

### Conclusions

The basic motif of a tetracoordinate germanium-acid ester, as claimed by Müller and Heinrich, was found to be restricted to the most sterically demanding substituents and thus appears to be a special case of a germanium–diol interaction.

Using diols whose structures are closer to the binding motifs that are typical for carbohydrates, electroneutral ger-



**Figure 5** ORTEP diagram of  $\text{Ge}(\text{EthdH}_{-1})_2\text{Cl}_2$  (**5**). Displacement ellipsoids are drawn at the 50% probability level.

Selected bond distances in Å: Ge-Cl 2.2173(5), Ge-O1 1.8402(11), Ge-O2 2.0144(13) and angles in °: Cl-Ge-O1 93.68(4), Cl-Ge-O2 173.81(4), Cl-Ge-Cl<sup>i</sup> 95.18(2), Cl-Ge-O1<sup>i</sup> 96.25(5), Cl-Ge-O2<sup>i</sup> 90.84(8), O1-Ge-O2 83.20(5), O1-Ge-O1<sup>i</sup> 165.25(7), O1-Ge-O2<sup>i</sup> 85.85(7), O2-Ge-Cl<sup>i</sup> 90.48(4), O2-Ge-O2<sup>i</sup> 83.98(5). <sup>i</sup> -x-y, -y, -z+1/3.

manium compounds can be obtained as well. In the case of silicon, the attempted spiro-bis(alkylenedioxy) compounds are isolated both monomerically and dimerically, the latter bonding mode reflecting a kind of residual Lewis acidity of the silicon centre.

In this work, the larger germanium atoms reveal a more differentiated chemistry. Monomers are lacking in the case of the sterically less demanding furanose analogs, but dimers such as those formed by silicon were obtained. However, though monomers of the bis[diolato(2-)] type do not form, germanium was found in mononuclear species of a unique structure. Being both electroneutral and higher-coordinated, in **3–5** the germanium atom binds at least one diolato(1-) ligand, and thus shows a structure that usually appears to play a role in the decomposition of carbohydrate complexes of various metals on acid addition. Hopefully, these species, which show the same degree of protonation as, for example, orthosilicic acid at physiological conditions, may contribute to the quest for silica transport forms in silicifying organisms.

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