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Synthetic studies and structural aspects of some metallacyclic compounds of germanium(IV) incorporating nitrogen, oxygen and sulfur:1. Reactions of germanium(IV) isopropoxide with diols and crystal structure of a diolato bridged germanium(IV) compound $[Ge_2(O_2C_2H_4)_4]$[†]

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Germanium(IV) diolates of the type $[(OPr^i)_{4\text{-}2n}Ge(O\text{–}G\text{–}O)_n]$ (n = 1, 2) have been prepared by the reaction of $Ge(OPr^i)_4$ with the corresponding diols in 1:1 and 1:2 molar ratios in anhydrous benzene. All these compounds are colourless viscous liquids except the bis(ethanediolato)germanium(IV), which is a white solid. They have been characterised by elemental analysis and IR and NMR (^1H and ^{13}C) spectroscopy. Prismatic crystals of $[Ge_2(O_2C_2H_4)_4]$ were separated out when $[(OPr^i)_2Ge(O_2C_2H_4)]$ was kept for about 3 weeks at room temperature. Single crystal X-ray diffraction study indicates that it is a unique diolato bridged compound in which the geometry around the germanium atom is a distorted trigonal bipyramid of oxygen atoms which belong to one chelating diolato-O,O′ and to a second η^1–O, $\mu_2(\eta^1$–O′) bound diolato group.

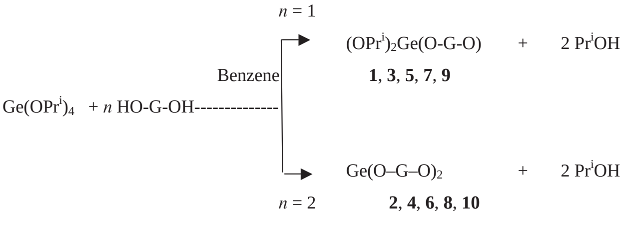
Keywords: diolato ligand, germanium, pentacoordination, digermoxan ring, X-ray structure analysis

Of the alkoxy- and glycoxy derivatives of tetravalent elements (group14 as well as 4) which have been extensively studied[1-2] from spectroscopic as well as structural points of view, those of germanium have received much less attention. Although penta[3-6] and hexa[7-10] coordinated derivatives of even germanium with complex organic moieties have been reported, the alkoxy derivatives generally prefer a tetracoordinated structure[11-14] even with alkoxyalkanols as shown in a recent publication.[14]

In this paper, a crystallographically characterised pentacoordinate diolate bridged derivative, $[Ge_2(O_2C_2H_4)_4]$, is being reported for the first time as part of a detailed physico-chemical study of the diolate derivatives of germanium(IV).

Results and discussion

Reactions of $Ge(OPr^i)_4$ with a variety of glycols in 1:1 and 1:2 molar ratios in anhydrous benzene yield the compounds $(OPr^i)_2Ge(O\text{–}G\text{–}O)$ (**1**, **3**, **5**, **7**, **9**) or $Ge(O\text{–}G\text{–}O)_2$ (**2**, **4**, **6**, **8**, **10**), respectively. Although the synthesis of derivatives, **2**, **4** and **8** only had been described[15] earlier in 1963 without any physico-chemical or spectroscopic data from our laboratories using $Ge(OEt)_4$ as precursor, now for the sake of further comparative spectroscopic studies these have been resynthesised from $Ge(OPr^i)_4$:



$$Ge(OPr^i)_4 + n\,HO\text{-}G\text{-}OH \xrightarrow{\text{Benzene}} \begin{cases} n = 1: & (OPr^i)_2Ge(O\text{-}G\text{-}O) + 2\,Pr^iOH \quad \mathbf{1, 3, 5, 7, 9} \\ n = 2: & Ge(O\text{–}G\text{–}O)_2 + 2\,Pr^iOH \quad \mathbf{2, 4, 6, 8, 10} \end{cases}$$

G	$(CH_2)_2$	CH_2CHMe	CH_2CHEt	CHMeCHMe	$(CH_2)_5$
	1, **2**	**3**, **4**	**5**, **6**	**7**, **8**	**9**, **10**

These reactions are quite facile as well as quantitative. The liberated isopropanol was estimated oxidimetrically until the distillate showed its absence. The excess of solvent was then removed under reduced pressure. All the above compounds are colourless viscous liquids, soluble in common organic solvents, except bis(ethanediolato)germanium(IV) (**2**), which is a solid and soluble only in polar solvents. Molecular weight measurements (ebullioscopic) indicated the monomeric nature of these compounds. All the products are thermally unstable and disproportionate or are decomposed on distillation under reduced pressure.

In the special case of compound **1** this disproportionation reaction yielded an interesting pentacoordinated compound. When **1** is left for 2–3 weeks at room temperature, shiny crystals of the disproportionation product $[Ge_2(O_2C_2H_4)_4]$ **(2)** are obtained:

$$\underset{\mathbf{1}}{4\,(OPr^i)_2Ge(O_2C_2H_4)} \longrightarrow \underset{\mathbf{2}}{Ge_2(O_2C_2H_4)_4} + 2\,Ge(OPr^i)_4$$

The product **(2)** (m.p. 108–110°C) is insoluble in common organic solvents, except chloroform in which it is sparingly soluble. The IR, ^1H and ^{13}C NMR spectra of compounds **1**–**10** have been recorded and summarised in Table 1.

IR spectra: Assignments of IR bands have been made by comparing the spectra with those of the free ligands and related compounds.[16,17] A medium-sized band in the region 3100–3300 cm^{-1} in the free ligands due to ν(OH) is absent in the IR spectra of the complexes **1**–**10**, indicating deprotonation of glycols. This is further suppported by the appearance of a new medium to strong band in the region 850–875cm^{-1} assigned to ν (Ge–O). A medium to strong band in the region 1080–1055 cm^{-1} has been assigned to ν(C–O) of the diolate moiety.

^1H NMR spectra: A comparison of the ^1H NMR spectra of the complexes with those of the free diols reveals that the singlet observed for the –OH proton of the diols was missing in the corresponding complexes indicating deprotonation of ligands and formation of Ge–O bonds. In the 1:1 complexes **1**, **3**, **5**, **7** and **9** the methyl protons of the isopropoxy moiety appear in the range δ 1.06–1.25 ppm as doublets and the CH proton appears in the range δ 3.43–3.92 ppm as a broad band. In all the complexes OCH_2 or OCH protons of the diol appear in the range δ 3.10–4.57 ppm or δ 4.30–4.57 ppm, respectively, as a broad band. All other proton resonances have been observed at their expected positions.

^{13}C NMR spectra: The ^{13}C NMR spectra of all the above complexes exhibit their expected characteristic peaks. The CH_3 signals of the isopropoxy group in the 1:1 complexes appear in the range δ 24.6–25.7 ppm while OCH_2 and OCH carbon signals of the diolate moieties appear in the region δ 63.4–75.0 ppm. No significant change in the chemical shifts was observed for 1:1 and 1:2 compounds formed from the same diol.

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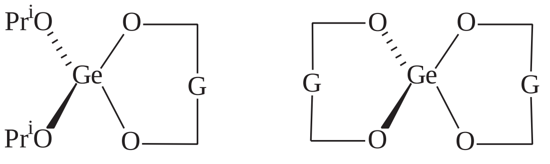
[†] Dedicated to Professor Ekkehard Lindner on the occasion of his 70th birthday.

Table 1 Spectroscopic data of compounds **1–10**

Compound	IR $[cm^{1}]$ ν(C–O) (^{i}PrO)	ν(C–O) (O–G–O)	ν(Ge–O)	^{1}H NMR δ[ppm] (^{i}PrO)	(O–G–O)	^{13}C NMR δ[ppm] (^{i}PrO)	(O–G–O)
1	1025, m	1075, s	855, s	1.19 d(CH_3) 3.69 s (CH)	3.10 br (OCH_2)	24.9 (CH_3) 63.9 (CH)	63.6 (OCH_2)
2	–	1065, s	850, s	–	3.10 br (OCH_2) 3.83 br (OCH_2)	–	63.4 (OCH_2)
3	1015, m	1070, m	870, m	1.25 d (CH_3) 3.72-3.92 m (CH)	1.11 d (CH_3) 3.55 br (CH_3) 4.50 br (CH)	24.6 (CH_3) 63.5 (CH)	18.4 (CH_3) 67.3 (CH) 67.8 (OCH_2)
4	–	1055, s	860, s	–	1.01 d (CH_3) 3.59 br (CH_2) 4.57 br (CH)	–	18.4 (CH_3) 67. 3 (CH) 67.8 (OCH_2)
5	1020, s	1080, s	850, s	1.20 d (CH_3) 3.62 br (CH)	0.99 t (CH_3) 1.55 q (CH_2) 3.54 br (OCH_2) 4.55 br (OCH)	25.7 (CH_3) 63.6 (CH)	9.6 (CH_3) 24.6 (CH_2) 65.6 (OCH) 73.3 (OCH_2)
6	–	1060, m	875, s	–	0.95 t (CH_3) 1.52 q (CH_2) 3.61 br (OCH_2) 4.50 br (OCH)	–	9.7 (CH_3) 25.1 (CH_2) 66.1 (OCH) 74.0 (OCH_2)
7	1018, m	1070, m	870, s	1.06 d (CH_3) 3.43 br (CH)	1.00 br (CH_3) 4.30 br (OCH)	25.0 (CH_3) 65.5 (CH)	14.4 (CH_3) 71.6 (OCH)
8	–	1060, m	860, s	–	1.00 br (CH_3) 4.33 br (OCH)	–	14.8 (CH_3) 71.5 (OCH)
9	1025, m	1075, m	865, s	1.14 d (CH_3) 3.58 br (CH)	3.33 br (γ-CH_2) 4.20 br (β-CH_2) 4.44 br (OCH_2)	25.4 (CH_3) 63.9 (CH)	58.4 (γ-CH_2) 69.5 (β-CH_2) 74.6 (OCH_2)
10	–	1060, m	870, s	–	3.42 br (γ-CH_2) 4.23 br (β-CH_2) 4.57 br (OCH_2)	–	66.4 (γ-CH_2) 71.5 (β-CH_2) 75.0 (OCH_2)

Thus, on the basis of elemental analyses, IR and NMR spectral data, the following tentative structures (Fig.1) may be proposed for compounds of the type $[(OPr^{i})_2Ge(O–G–O)]$ (**1**, **3**, **5**, **7**, **9**) (a) and $[Ge(O–G–O)_2]$ (**2**, **4**, **6**, **8**, **10**) (b)].

Crystal structure of $[Ge_2(O_2C_2H_4)_4]$ **(2):** Single crystals of $Ge_2(O_2C_2H_4O)_4$ (**2'**) suitable for X-ray diffraction studies were obtained when the viscous product **1** is kept at the room temperature for 2–3 weeks. The results of the structural determination are summarised in Table 2 and the molecular structure of $Ge_2(OCH_2CH_2O)_4$ is centrosymmetric with the most important bonding parameters is given in Fig.2. This structural analysis of $Ge_2(OCH_2CH_2O)_4$ confirms a planar four-membered heterocycle of two alternating germanium and two oxygen atoms (sum of angles = 360.0°C). Each oxygen atom (O(12) and O(12A)) belongs to the bridging and chelating five-membered diolato ligand with an envelope conformation, where the atom C(22) lies above the ring plane. Each germanium atom (Ge(1)) possesses a distorted trigonal-bipyramidal configuration, with O(12), O(21) and O(22A) in the trigonal plane and O(11) and O(12A) in the apical positions (O(11)–Ge–O(12A) = 174.5(2)). The second diolato ligand acts only by chelating, and has a less distorted envelope conformation, whereby atom C(11) lies outside of the plane. The Ge–O bonds within the digermoxane ring differ very much (Ge–O(12) = 1.835(4), Ge–O(12A) = 2.082(4) Å). They are significantly larger than the Ge–O bonds of the chelating diolate system outside of the four-membered ring ($Ge–O_n \approx 1.77$ Å).



(a) (b)

Fig.1 Proposed structures for compounds $[(OPr^{i})_2Ge(O–G–O)]$ (a) and $[Ge(O–G–O)_2]$ (b).

Table 2 Crystallographic data of $Ge_2(OCH_2CH_2O)_4$ (**2**)

Empirical formula	$C_8H_{16}Ge_2O_8$
Mol wt.	385.43
Size	0.16 × 0.12 × 0.08 mm
Colour and habit	Colourless prismatic
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a[Å]	8.2695(9)
b[Å]	7.6208(10)
c[Å]	9.9659(12)
∃(°)	102.450(6)
V (Å)^3	613.28(13)
Z	2
$D_{calc.}$ (g/cm^3)	2.0877(4)
Absorption coefficient (mm^{-1})	4.931
F(000)	384
Diffractometer	Nonius Kappa CCD
Radiation	Mo-K_α (λ = 0.71073 Å)
Scan type	Area detector
Temperature (K)	200(2
2θ range	6.80 to 50.00°
Index ranges	$-9 \le h \le 9$, $-9 \le k \le 9$, $-11 \le l \le 11$,
Reflections collected	6203
Independent reflections	1076 (R_{int} = 0.1054)
Observed reflections	778 ($F > 4\Phi(F)$)
Absorption correction	Numerical
Max./min. transmission	0.7098/0.5201
System	SHELXS-97
Solution	Direct methods
Refinement	Full-matrix least squares
Hydrogen atoms	Riding
Weighting scheme, x, y	0.0447, 2.0778
Data / restraints / parameters	1076 / 0 / 82
Data-to-parameter-ratio	13.1 : 1 {9.5 : 1 [$F > 4\Phi(F)$]}
R index [$F > 4\Phi(F)$]	$R1$ = 0.0477, $wR2$ = 0.0962
R index (all data)	$R1$ = 0.0789, $wR2$ = 0.1233
GOOF	1.097

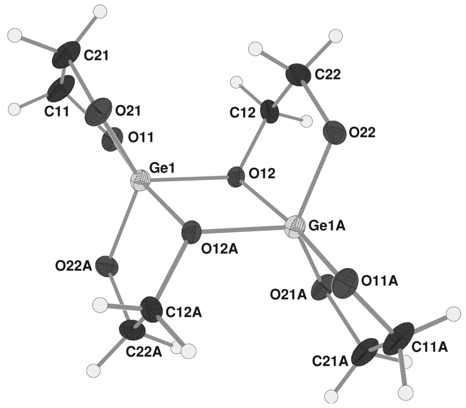


Fig. 2 Molecular structure of $[Ge_2(O_2C_2H_4)_4]$; selected bond lengths [Å] and angles [°]: Ge–O(12) 1.835(4), Ge–O(12A) 2.082(4), Ge–O(11) 1.782(4), Ge–O(21) 1.775(5), Ge–O(22A) 1.757(4), C(11)–O(11) 1.426(9), C(21)–O(21) 1.452(8), C(11)–C(21) 1.476(11), C(12)–O(12) 1.456(7), C(22)–O(22) 1.443(8), C(12)–C(22) 1.504(10); O(12)–Ge–O(12A) 76.07(19), Ge–O(12)–Ge(A) 103.93(19), O(11)–Ge–O(12) 99.2(2), Ge–O(12)–C(12) 121.2(4), O(11)–Ge–O(21) 94.1(2), O(11)–Ge–O(22A) 100.5(2), O(21)–Ge–O(22A) 124.4(3), O(21)–Ge–O(12A) 85.98(18), O(12A)–Ge–O(22A) 83.92(18), O(11)–Ge–O(12A) 174.5(2).

Experimental

All experimental manipulations were performed in a moisture free environment. Diols, isopropanol and benzene were made anhydrous by using literature methods.[18,19] $Ge(OPr^i)_4$ was freshly prepared by a procedure reported earlier[20] and distilled prior to use. Germanium was estimated as GeO_2[21] and isopropanol in the azeotrope by an oximetric method.[22]

CAUTION: All operations were carried out with due care because of the hazardous nature of benzene and other solvents.

IR spectra were recorded as Nujol mulls on a Nicolet Magna-550 spectrophotometer in the range 4000–400 cm^{-1}. NMR spectra (^1H and ^{13}C) were recorded on a 90 MHz JEOL FX 90Q spectrometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$ (using D_2O lock). Molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer fitted in a glass assembly in anhydrous benzene.

Preparation of $(OPr^i)_2Ge(OCH_2CH_2O)$ **(1)**: A benzene suspension of ethane 1,2-diol (0.19 g, 3.0 mmol) was added dropwise to a benzene solution of $Ge(OPr^i)_4$ (0.93 g, 3.0 mmol). Initially a white thin layer began to form. After some time, a clear solution was obtained. It was refluxed for about 4h and the liberated Pr^iOH was continuously fractionated out azetropically with benzene. The Pr^iOH content of the azeotrope was estimated periodically by an oxidimetric method so as to monitor the progress of the reaction. When the azeotrope showed negligible presence of Pr^iOH, the reaction was stopped and the excess solvent was removed under reduced pressure to yield a colourless viscous liquid; yield 0.72 g, 96%. – $C_8H_{18}O_4Ge$ calcd.: Ge 28.9; OPr^i 47.1; found: Ge 29.0; OPr^i 47.0.

All other monodiolato germanium(IV) complexes of the type $(OPr^i)_2Ge(O–G–O)$ (**3**, **5**, **7**, **9**) were prepared using a similar route. Their synthetic details and analytical data are summarised in Table 3.

Preparation of $Ge(O_2C_2H_4)_2$ **(2)**: A benzene suspension of (~10 ml) of ethane 1,2-diol (0.39 g, 6.3 mmol) was added dropwise to a benzene solution of $Ge(OPr^i)_4$ (0.98 g, 3.2 mmol). This mixture was refluxed for about 4h. and liberated Pr^iOH was estimated periodically. When the azeotrope showed the negligible presence of Pr^iOH, the reaction was stopped and the excess solvent was stripped off *in vacuo* to yield a white solid; yield 0.59 g, 96%. – $C_4H_8O_4Ge$ calcd.: Ge 37.7; found: Ge 37.6.

Similarly all other bisdiolato complexes $Ge(O–G–O)_2$ (**4**, **6**, **8**, **10**) were prepared and the results are summarised in Table 3.

Preparation of crystals of $[Ge_2(O_2C_2H_4)_4]$ **(2)**: On setting aside the compound $[(OPr^i)_2Ge(O_2C_2H_4)]$ (**1**) for 2-3 weeks, shiny crystals of $[Ge_2(O_2C_2H_4)_4]$ were obtained, possibly due to the disproportionation

Table 3 Synthetic and analytical data for the compounds $[(OPr^i)_2Ge(O\text{-}G\text{-}O)]$ (**1**, **3**, **5**, **7**, **9**) and $[Ge(O\text{-}G\text{-}O)_2]$ (**2**, **4**, **6**, **8**, **10**)

.		Reactants/g	Molar ratio	Product	Pr^iOH found (calcd.)	Yield/%	Analysis % found (calcd)		Mol. wt. found (calcd.)
	(a) (b)	Ge $(OPr^i)_4$ Ligand					Ge	OPr^i	
1	(a)	0.93							
	(b)	$HOCH_2CH_2OH$, 0.19	1:1	$(OPr^i)_2Ge(OCH_2CH_2O)$	0.35 (0.36)	96	29.0 (28.9)	47.0 (47.1)	258 (251)
2	(a)	0.98							
	(b)	$HOCH_2CH_2OH$, 0.39	1:2	$Ge(OCH_2CH_2O)_2$	0.75 (0.76)	96	37.6 (37.7)	–	_* (193)
3	(a)	0.95							
	(b)	$HOCH_2CH(CH_3)OH$, 0.23	1:1	$(OPr^i)Ge\{OCH_2CH(CH_3)O\}$	0.36 (0.37)	96	27.4 (27.4)	44.4 (44.6)	260 (265)
4	(a)	0.84							
	(b)	$HOCH_2CH(CH_3)OH$, 0.41	1:2	$Ge\{OCH_2CH(CH_3)O\}_2$	0.65 (0.66)	95	32.9 (32.8)	–	228 (221)
5	(a)	1.10							
	(b)	$HOCH_2CH(C_2H_5)OH$, 0.32	1:1	$(OPr^i)_2Ge\{OCH_2CH(C_2H_5)O\}$	0.42 (0.43)	96	26.1 (26.0)	42.3 (42.4)	271 (279)
6	(a)	1.17							
	(b)	$HOCH_2CH(C_2H_5)OH$, 0.68	1:2	$Ge\{OCH_2CH(C_2H_5)O\}_2$	0.90 (0.91)	96	29.0 (29.2)	–	257 (249)
7	(a)	1.04	1:1			96			
	(b)	$HO(CH_3)CHCH(CH_3)OH$, 0.31		$(OPr^i)_2Ge\{O(CH_3)CHCH(CH_3)O\}$	0.40 (0.41)		26.1 (26.0)	42.2 (42.3)	266 (279)
8	(a)	1.18							
	(b)	$HO(CH_3)CHCH(CH_3)OH$, 0.69	1:2	$Ge\{O(CH_3)CHCH(CH_3)O\}_2$	0.91 (0.92)	97	29.1 (29.2)	–	265 (249)
9	(a)	1.07							
	(b)	$HOCH_2(CH_2)_3CH_2OH$, 0.36	1:1	$(OPr^i)_2Ge\{OCH_2(CH_2)_3CH_2O\}$	0.41 (0.42)	97	24.9 (24.8)	40.1 (40.3)	282 (293)
10	(a)	0.95							
	(b)	$HOCH_2(CH_2)_3CH_2OH$, 0.64	1:2	$Ge\{OCH_2(CH_2)_3CH_2O\}_2$	0.72 (0.74)	96	26.3 (26.2)	–	285 (277)

*Insoluble

reaction mentioned above; quantitative yield. – $C_8H_{16}O_8Ge_2$ calcd.: Ge 37.7 %; found 37.8 %.

X-ray structure determination: A colourless prismatic crystal of $[Ge_2(O_2C_2H_4)_4]$ was mounted on a glass fibre. An image-plate area detector diffractometer, with area scans choosen to give a complete asymmetric unit, was used for data collection. Cell refinements gave cell constants corresponding to monoclinic cell whose dimension are given in Table 2 along with other experimental parameters. An absorption correction of 4.931 mm^{-1} was applied. The structure was solved by direct methods[23] and the structure was refined using the win GX version[24] of SHELX-97.[25] The final cycle of full matrix least square refinement was based on 1076 observed rejections [777 for ($F > 4\ \sigma\ (F)$)] and 82 variable parameters.[26]

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26 Further crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-207034 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]