SHORT PAPER

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Synthesis and spectroscopic characterisation of some neutral tetracoordinated germanium (IV) alkoxyalkanolates

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Compounds of the type, $[Ge(OPr^i)_{4-n}(OCH_2CH_2OR)_n]$, (where R = Me, Et, *n*-Bu and *n* = 1-4) have been synthesised in high yields by the interactions of germanium tetraisopropoxide with alkoxyalkanols ($HOCH_2CH_2OR$) in different stoichiometries in refluxing anhydrous benzene, and are monomeric in refluxing benzene. All these compounds can be purified by distillation under reduced pressure. IR and NMR (^1H and ^{13}C) spectral studies indicate a tetrahedral geometry around the germanium atom.

Keywords: germanium tetraisopropoxide, alkoxyalkanol, IR and NMR spectra

The majority of germanium (IV) compounds prefer tetrahedral geometry with ligands containing nitrogen, oxygen and/or sulfur donor atoms.[1-5] Crystal structures of $[Ge\{S(CH_2)_2S(CH_2)_2S\}_2]$ and $[Ge\{S(CH_2)_2O(CH_2)_2S\}_2]$, containing even some bifunctional potentially tridentate ligands, exhibit tetrahedral geometry around the germanium (IV) atoms,[4] indicating actually bidentate ligation in every case.

However, more recently Pastor *et al*. reported[6] the first crystallographic evidence for a neutral hypervalent germanium (IV) compounds with sulphur- and selenium-induced hexa-coordination of germanium in the spirocyclic complexes, $[Ge\ \{2,2'\text{-}S(4,6\text{-}Bu^t{}_2C_6H_2O)_2\}_2]$ and $\{Ge\ (2,2'\text{-}Se(4,6\text{-}Bu^t{}_2C_6H_2O)_2\}_2]$.

Amongst the alkoxy derivatives of various elements described from these and other laboratories,[7] metal alkoxyalkanolates represent an interesting class of compounds due to the monodentate and anisobidentate behaviour of this ligand moiety. For example, the crystal structure of a remarkable decameric compound $[Y_{10}(OC_2H_4OMe)_{30}]$ exhibits bidentate behaviour of the alkoxyalkanol moiety leading to seven coordination around each yttrium atom.[8]

All the corresponding alkoxyalkanol derivatives of germanium(IV) exhibit tetrahedral geometry around germanium, indicating bonding through oxygen of the OH group only of alkoxyalkanols.

In this paper, we report the synthesis and characterisation of some new germanium (IV) alkoxyalkanolates of the type, $[Ge(OCH_2CH_2OR)_n(OPr^i)_{4-n}]$.

Results and discussion

Compounds of the type, $[Ge(OCH_2CH_2R)_n(OPr^i)_{4-n}]$ have been prepared by the reactions of germanium tetraisopropoxide and alkoxyalkanol in different molar ratios in refluxing anhydrous benzene as shown in Eqn (1):

$$[Ge(OPr^i)_4] + n\ HOCH_2CH_2OR \rightarrow [Ge(OCH_2CH_2OR)_n(OPr^i)_{4-n}] + nPr^iOH \quad (1)$$

$$\text{(where R = Me, Et and Bu}^n;\ n = 1\text{-}4)$$

All these reactions are quantative and the liberated isopropanol could be removed as a benzene–isopropanol azeotrope in ~4h. The completion of these reactions was checked by estimating (iodometrically)[9] the liberated isopropanol in the azeotrope. All the products are colourless liquid which can be distilled *in vacuo*. The boiling points of all these compounds increase with their molecular weights. Molecular weight measurements in boiling benzene show the complexes to be monomeric.

IR spectra: IR spectra of these redistilled compounds were interpreted by comparing their spectra with that of the free ligands.[10] A medium intensity bands at 3450 cm^{-1} in the free ligands due to ν(OH) is absent in the IR spectra of all these complexes, indicating deprotonation of the alkoxyalkanol and the formation of a metal–ligand bond through the oxygen atom. This is further supported by the appearance of a new broad band due to ν(Ge-O)[11] in the region 860–880 cm^{-1}. Broadening of this band in all the above complexes may be due to the different ligand environments around Ge(IV). It is worth mentioning here that in the case of pure $[Ge(OPr^i)_4]$ a sharp band due to ν(Ge–O) was observed at 855 cm^{-1}. The medium

Table 1 IR spectral data (cm^{-1}) of Ge(IV) complexes

Compd no.	Compound	Isopropoxy moiety ν(C–O)	ν(Ge–O)	Alkoxyalkanolate moiety ν(C–O)	Alkoxyalkanolate moiety ν(C–O–C)
1	$[Ge(OCH_2CH_2OMe)(OPr^i)_3]$	1005	875	1070	1025
2	$[Ge(OCH_2CH_2OMe)_2(OPr^i)_2]$	1005	860	1055	1020
3	$[Ge(OCH_2CH_2OMe)_3(OPr^i)]$	1015	860	1090	1055
4	$[Ge(OCH_2CH_2OMe)_4]$	–	865	1050	1030
5	$[Ge(OCH_2CH_2OEt)(OPr^i)_3]$	1010	880	1065	1045
6	$[Ge(OCH_2CH_2OEt)_2(OPr^i)_2]$	1015	875	1080	1040
7	$[Ge(OCH_2CH_2OEt)_3(OPr^i)]$	1015	875	1090	1035
8	$[Ge(OCH_2CH_2OEt)_4]$	–	870	1070	1025
9	$[Ge(OCH_2CH_2OBu)(OPr^i)_3]$	1005	880	1095	1040
10	$[Ge(OCH_2CH_2OBu)_2(OPr^i)_2]$	1010	870	1070	1020
11	$[Ge(OCH_2CH_2OBu)_3(OPr^i)]$	1015	875	1080	1015
12	$[Ge(OCH_2CH_2OBu)_4]$	–	860	1080	1030

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 ^1H NMR spectral data (δ ppm) of Ge(IV) complexes

Compd no.	Isopropoxy moiety		Alkoxyalkanolate moiety
	CH_3	OCH	
1	1.28 d (18H)	4.59–4.72 m (3H)	3.48 s (3H, $OC\mathbf{H}_3$); 3.64–4.12 m (4H, $OC\mathbf{H}_2C\mathbf{H}_2O$)
2	1.18 d (12H)	4.20–4.56 m (2H)	3.46 s (6H, $OC\mathbf{H}_3$); 3.54–3.98 m (8H, $OC\mathbf{H}_2C\mathbf{H}_2O$)
3	1.20 d (6H)	3.99–4.22 m (1H)	3.45 s (9H, $OC\mathbf{H}_3$); 3.48–3.96 m (12H, $OC\mathbf{H}_2C\mathbf{H}_2O$)
4	–	–	3.48 s (12H, $OC\mathbf{H}_3$); 3.64–3.84 m (16H, $OC\mathbf{H}_2C\mathbf{H}_2O$)
5	1.14 d (18H)	4.19–4.46 m (3H)	1.06 t (3H, $OCH_2C\mathbf{H}_3$); 3.31–3.58 m (6H, $OC\mathbf{H}_2C\mathbf{H}_2OC\mathbf{H}_2CH_3$)
6	1.15 d (12H)	4.18–4.35 m (2H)	1.05 t (6H, $OCH_2C\mathbf{H}_3$); 3.42–3.65 m (12H, $OC\mathbf{H}_2C\mathbf{H}_2OC\mathbf{H}_2CH_3$)
7	1.26 d (6H)	4.12–4.37 m (1H)	1.19 t (9H, $CH_2C\mathbf{H}_3$); 3.49–3.67 m (18H, $OC\mathbf{H}_2C\mathbf{H}_2OC\mathbf{H}_2CH_3$)
8	–	–	1.17 t (12H, $CH_2C\mathbf{H}_3$); (24H, $OC\mathbf{H}_2C\mathbf{H}_2OC\mathbf{H}_2CH_3$)
9	1.26 d (18H)	4.16–4.41 m (3H)	1.07t{3H,$O(CH_2)_3C\mathbf{H}_3$};3.38–4.10 m{10H, $OC\mathbf{H}_2C\mathbf{H}_2O(C\mathbf{H}_2)_3CH_3$}
10	1.20 d (12H)	4.22–4.78 m (2H)	1.04t{6H,$O(CH_2)_3C\mathbf{H}_3$};3.24–3.96m {20H, $OC\mathbf{H}_2C\mathbf{H}_2O(C\mathbf{H}_2)_3CH_3$}
11	1.16 d (6H)	4.10–4.46 m (1H)	0.99t{9H,$O(CH_2)_3C\mathbf{H}_3$};3.15–3.74m{30H, $OC\mathbf{H}_2C\mathbf{H}_2O(C\mathbf{H}_2)_3CH_3$}
12	–	–	1.02t{12H,$O(CH_2)_3C\mathbf{H}_3$};3.02-3.82m{ 40H, $OC\mathbf{H}_2C\mathbf{H}_2O(C\mathbf{H}_2)_3CH_3$}

Table 3 ^{13}C NMR spectral data (δ ppm) of Ge(IV) complexes

Compd no.	Isopropoxy moiety		Alkoxyalkanolate moiety
	CH_3	OCH	
1	24.6	62.2	58.4 ($\mathbf{C}H_3$); 64.2 ($O\mathbf{C}H_2CH_2OMe$); 71.1 ($OCH_2\mathbf{C}H_2OMe$)
2	24.9	61.8	58.6 ($\mathbf{C}H_3$); 64.4 ($O\mathbf{C}H_2CH_2OMe$); 72.0 ($OCH_2\mathbf{C}H_2OMe$)
3	24.2	62.0	57.8 ($\mathbf{C}H_3$); 63.8 ($O\mathbf{C}H_2CH_2OMe$); 71.4 ($OCH_2\mathbf{C}H_2OMe$)
4	-	-	58.6 ($\mathbf{C}H_3$); 64.4 ($O\mathbf{C}H_2CH_2OMe$); 71.6 ($OCH_2\mathbf{C}H_2OMe$)
5	25.8	61.4	22.03($\mathbf{C}H_3$);64.4($O\mathbf{C}H_2Me$);66.4($O\mathbf{C}H_2CH_2OEt$); 71.5 ($OCH_2\mathbf{C}H_2OEt$)
6	25.4	61.8	22.09($\mathbf{C}H_3$);64.9($O\mathbf{C}H_2Me$);66.6($O\mathbf{C}H_2CH_2OEt$); 71.9 ($OCH_2\mathbf{C}H_2OEt$)
7	25.2	61.2	22.11($\mathbf{C}H_3$);64.4($O\mathbf{C}H_2Me$);66.9($O\mathbf{C}H_2CH_2OEt$); 71.8 ($OCH_2\mathbf{C}H_2OEt$)
8	-	-	22.06($\mathbf{C}H_3$);64.2($O\mathbf{C}H_2Me$);66.3($O\mathbf{C}H_2CH_2OEt$); 71.2 ($OCH_2\mathbf{C}H_2OEt$)
9	26.2	61.8	14.3($\mathbf{C}H_3$);25.2{$OCH_2CH_2O(CH_2)_2\mathbf{C}H_2Me$}; 40.2{$OCH_2CH_2OCH_2\mathbf{C}H_2Et$};62.1{$OCH_2CH_2O\mathbf{C}H_2Pr$}; 65.7 {$O\mathbf{C}H_2CH_2OBu$}; 71.6 {$OCH_2\mathbf{C}H_2OBu$}
10	26.6	61.2	15.1($\mathbf{C}H_3$);25.4{$OCH_2CH_2O(CH_2)_2\mathbf{C}H_2Me$}; 40.6{$OCH_2CH_2OCH_2\mathbf{C}H_2Et$};62.9{$OCH_2CH_2O\mathbf{C}H_2Pr$}; 66.2 {$O\mathbf{C}H_2CH_2OBu$}; 72.2 {$OCH_2\mathbf{C}H_2OBu$}
11	25.9	61.6	14.6($\mathbf{C}H_3$);25.8{$OCH_2CH_2O(CH_2)_2\mathbf{C}H_2Me$}; 41.2{$OCH_2CH_2OCH_2\mathbf{C}H_2Et$};62.2{$OCH_2CH_2O\mathbf{C}H_2Pr$}; 65.3 {$O\mathbf{C}H_2CH_2OBu$}; 71.8 {$OCH_2\mathbf{C}H_2OBu$}
12	–	–	14.9($\mathbf{C}H_3$);26.2{$OCH_2CH_2O(CH_2)_2\mathbf{C}H_2Me$}; 41.5{$OCH_2CH_2OCH_2\mathbf{C}H_2Et$};62.8{$O.CH_2CH_2O\mathbf{C}H_2Pr$}; 65.6 {$O\mathbf{C}H_2CH_2OBu$}; 72.1 {$OCH_2\mathbf{C}H_2OBu$}

intensity bands observed in the region 1050–1095 cm^{-1} and 1015–1055 cm^{-1} are assigned to alkoxyalkanol ν(C–O) and ν(C–O–C), respectively. The isopropoxy ν(C–O) values have been observed in the region 1005–1015 cm^{-1} (Table 1).

^1H NMR spectra: The ^1H spectra of all these redistilled complexes exhibit characteristic peaks. In the ^1H NMR spectra of all these compounds, the hydroxyl protons resonances of free ligands are absent, indicating deprotonation of OH group of the alkoxyalkanol moiety and the formation of a Ge–O bond. No appreciable shift was observed in the position of alkoxyalkanol protons which were observed at their expected positions, ruling out the possibility of coordination through the oxygen atom of alkoxyalkanol moiety[12] (Table 2).

^{13}C NMR spectra: In the ^{13}C NMR spectra, the position and the number of alkoxyalkanol carbon signals are as expected (Table 3). The fact that no significant shift was observed in the position of alkoxy carbon of these ligand moieties further suggests that the alkoxyalkanol moiety[12] is bound to germanium atom in a monodentate fashion.

Experimental

All chemicals were of reagent grade and dried before use. All manipulations were performed in a moisture free environment. Germanium tetraisopropoxide was prepared according to the literature method.[13] Germanium[2] and isopropanol[9] were estimated as reported earlier.

Infrared spectra were recorded as Nujol mulls on Nicolet Magna-550 spectrophotometer in the range 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX 90Q spectrophotometer using TMS as an internal reference in $CDCl_3$ and $CHCl_3$, respectively. Molecular weight measurements were carried out by the elevation in boiling point method using a Beckmann thermometer (Einstellthermometer n-Beckmann, Labortherm-N, Skalenwert, 0.01 K, made in GDR) fitted in a glass assembly (supplied by JSGW India) in anhydrous benzene.

Preparation of [Ge(OCH_2CH_2OMe)(OPr^i)$_3$]: A benzene solution (~20 ml) of [Ge(OPr^i)$_4$] (1.06g, 3.43 mmol) was added to a benzene solution (~20 ml) of $HOCH_2CH_2OMe$(0.26g, 3.42 mmol). The contents were refluxed for 4h and the progress of the reaction was monitored by the determination of liberated isopropanol azeotropically with benzene. After the removal of the solvent under reduced pressure a colourless liquid was obtained (97% yield). The product (0.57g) was purified by distillation under vacuo at 86-88°C/0.4 mm to yield a colourless mobile distillate (0.46g, 81%) which can be considered to be quantitative considering the unavoidable loss which remains in distillation assembly.

All other complexes were prepared by a similar route and the details are summarised in Table 4.

Conclusion

On the basis of the molecular weight determinations, IR and NMR (^1H and ^{13}C) spectral studies a tetrahedral geometry around germanium atom has been proposed for the above germanium (IV) compounds derived from alkoxyalkanols (Fig.1). The quantitative yields of the final tetra-alkoxyalkanolates-alkoxides of germanium indicate that alcoholysis reactions are quite facile yielding the simple tetrahedral final products only.

Table 4 Synthetic and analytical data of Ge(IV) complexes

Compd no.	Reactants(g) a. Ge(OPr^i)$_4$ b. HOCH$_2$CH$_2$OR	Molar ratio	Pr^{i}OH (g) found (calcd.)	Yield %	OPr^i %	Ge %	Mol. wt. found (calcd.)	B.P. °C/mm (distillate (...g) from (...g) of the product)
1	a. 1.06 b. R = Me, 0.26	1 : 1	0.20 (0.20)	97	54.3 (54.5)	22.4 (22.3)	311 (324.92)	86–88/0.4 (0.46–0.57)
2	a. 1.36 b. R = Me, 0.67	1 : 2	0.52 (0.53)	97	34.4 (34.6)	21.4 (21.3)	329 (340.93)	88–90/0.1 (0.33–0.41)
3	a. 0.87 b. R = Me, 0.64	1 : 3	0.51 (0.51)	98	16.4 (16.5)	20.2 (20.3)	376 (356.94)	142–144/0.4 (0.29–0.35)
4	a. 0.78 b. R = Me, 0.77	1 : 4	0.61 (0.61)	97	–	19.4 (19.5)	380 (372.95)	166–168/0.4 (0.49–0.59)
5	a. 1.11 b. R = Et, 0.33	1 : 1	0.21 (0.21)	97	51.8 (52.2)	21.03 (21.04)	336 (338.94)	78–82/0.1 (0.65–0.80)
6	a. 1.10 b. R =Et, 0.64	1 : 2	0.43 (0.43)	98	31.2 (32.0)	19.3 (19.6)	385 (368.97)	80–85/0.1 (0.54–0.68)
7	a. 0.83 b. R = Et, 0.73	1 : 3	0.48 (0.49)	96	14.2 (14.8)	18.1 (18.2)	391 (399.00)	145–145/0.4 (0.46–0.57)
8	a. 0.81 b. R =Et, 0.95	1 : 4	0.63 (0.63)	97	–	16.8 (16.9)	428 (429.03)	178–180/0.4 (0.50–0.61)
9	a. 1.08 b. R = Bu, 0.41	1 : 1	0.21 (0.21)	96	48.0 (48.3)	19.7 (19.8)	378 (367.00)	85–88/0.1 (0.69–0.83)
10	a. 1.07 b. R = Bu, 0.82	1 : 2	0.42 (0.42)	98	27.3 (27.4)	17.0 (17.1)	410 (425.09)	89–91/0.1 (0.49–0.62)
11	a. 0.97 b. R = Bu, 1.11	1 : 3	0.56 (0. 57)	99	11.9 (12.2)	14.9 (15.0)	470 (483.18)	115–118/0.1 (0.71–0.81)
12	a. 0.84 b. R = Bu, 1.29	1 : 4	0.66 (0.66)	98	–	13.3 (13.4)	584 (541.27)	122–125/0.1 (0.64–0.74)

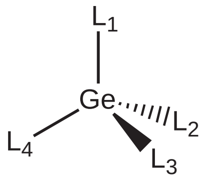

Fig.1 Proposed structure of [Ge(OCH2CH2OR)*n*OPri)4-*n*] {where L$_1$=OPr^i, L$_2$=L$_3$=L$_4$ = OCH$_2$CH$_2$OR; L$_1$ = L$_2$ = OPr$_i$, L$_3$ = L$_4$ = OCH$_2$CH$_2$OR ; L$_1$ = L$_2$ = L$_3$ = OPr$_i$, L$_4$ = OCH$_2$CH$_2$OR ; L$_1$ = L$_2$ = L$_3$ = L$_4$ = OCH$_2$CH$_2$OR and R = Me, Et and n-Bu ; *n* = 1-4}

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References

1 (a) D.C. Bradley, R.C. Mehrotra and D.P. Gaur, *Metal alkoxides*, Academic Press, London, 1978; (b) R.C. Mehrotra, R. Bohra and D.P. Gaur, *Metal β-diketonates and Allied Derivatives*, Academic Press, London, 1978.
2 D.C. Bradley, L. Kay and W. Wardlaw, *J. Chem. Soc.*, 1956, 4916.
3 T. Tanaka, G. Matsubayashi, A. Shimizu and S. Matsuo, *Inorg. Chim. Acta*,1969, **3,** 187.
4 D.H. Chen, H.C. Chiang and C.H. Ueng., *Inorg. Chim. Acta*,1993, **208,** 99.
5 J.E. Drake, A.G. Mislankar and J. Yang, *Inorg. Chem.*,1992, **31,** 5543.
6 (a) S.D. Pastor, V. Huang and N. Rahni, *Inorg. Chem.*,1997, **36,** 5966; (b) T. Thompson, S.D. Pastor and G. Rihs, *Inorg. Chem.*,1999, **38,** 4163.
7 D.C. Bradely, R.C. Mehrotra, I.P. Rothwell and A. Singh, *Alkoxo and Aryloxo Derivatives of Metals*, Academic Press, San Diego, 2001.
8 O. Poncelet, L.G. Hubert-Pfalzgraf, J.C. Daran, and R. Astier, *J. Chem. Soc., Chem. Commun.*, 1989, 1846.
9 D.C. Bradley, F.M.A. Halim and W. Wardlaw, *J. Chem. Soc.*, 1950, 3450.
10 R.M. Silverstein, G. Clayton, T.C. Morril, *Spectrometric Identification of Organic Compounds*, Vth Edn, 1991.
11 A. Singh, A.K. Rai and R.C. Mehrotra, *J. Organomet. Chem.*, 1973, **57,** 301.
12 N. Sharma, R.K. Sharma, R. Bohra, J.E. Drake, M.B. Hursthouse and M.E. Light, *J. Chem. Soc., Dalton Trans.*, 2002, 1631.
13 D.L. Tabern, W.R. Orndorff and L.M. Dennis, *J. Am. Chem. Soc.*, 1925, **47,** 2039.