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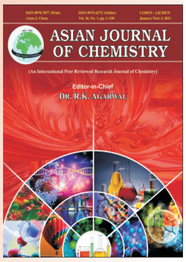

Synthesis and Characterization of Some New Metallo-Organic Derivatives of Germanium(IV)†

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Compounds of the type $GeG_n(OR)_{4-2n}$ [where G = $O(CH_2)_2S(CH_2)O$, $S(CH_2)_2O(CH_2)_2S$, $S(CH_2)_2S(CH_2)_2S$; R = Et, Pr^i and n = 1, 2] have been prepared by the reaction of $Ge(OR)_4$ with 2-hydroxyethyl sulfide, 2-mercaptoethyl ether and 2-mercaptoethyl sulfide in 1:1 and 1:2 molar ratios in refluxing anhydrous benzene. All these complexes are white sticky solid in appearance. After purification and spectral analyses (IR and ^1H and ^{13}C NMR) tetra coordination geometry is proposed around germanium atom.

Keywords: Metallo-organic compounds, Germanium alkoxides, Bifunctional tridentate ligands.

INTRODUCTION

In spite of the extensive synthetic and structural studies of metallo-organic derivatives of group 14 elements, germanium has received less attention[1,2]. Metallo-organic compounds of germanium have been the subject of considerable research interest due to its diverse structural features[3] and wide range of technological applications in industries[4]. These types of complexes have been well established as good precursors for metal oxide ceramic materials using sol-gel/MOCVD processes[5]. Germanium alkoxides as well as its other modified derivatives are quite often used to fabricate the thin film of germania[6] and its nano-wires containing visible photo luminescent material[7]. An appreciable contribution of GeO_2 in borosilicate glasses and in its other analogue glass ceramics has been reported by Darwish *et al*[8]. A biologically active nanocomposite powdered material of magnesium oxide-germanium dioxide has been well documented[9].

On the other hand, in addition to the structural variation, very recent coordination complex of gemanium(IV) has been shown as an efficient basic catalyst[10]. Though, germanium(IV) complexes are well understood to adopt tetrahedral geometry[11] but, some recent reports of the last decade are revealing the distorted tetrahedral configuration around the germanium(IV) *e.g.* germanium tetra tertiary butoxide[12] and $[Ge\{S(CH_2)_2S(CH_2)_2S\}_2]$ and $[Ge\{S(CH_2)_2O(CH_2)_2S\}_2]$[13]. Distortion may be attributed to the formation of the two eight membered chelating rings and to the interaction between germanium and the free oxygen or sulphur of the ligands. Evidently, Alekseev *et al.*[14] reported a distorted boat shaped eight membered ring containing germanium complex.

Therefore, in view of the above attracting features of germanium chemistry, we are reporting the synthesis and characterization of some new germanium(IV) derivatives of the type $GeG_n(OR)_{4-2n}$ along with only two known compounds[13] *via* different synthetic route.

EXPERIMENTAL

All chemicals were of reagent grade and dried before use. All manipulations were performed in a moist free environment. $Ge(OR)_4$ {where R = Et, Pr^i} were prepared according to the literature method[15]. Germanium[16], ethanol and isopropanol[17] were estimated as reported earlier. Infrared spectra were recorded as Nujol mull 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 Backmann thermometer (Einstell-thermometer *n*-Beckmann) in anhydrous benzene.

Preparation of $(OEt)_2Ge\{(OCH_2CH_2)_2S\}$: To a benzene solution of $Ge(OEt)_4$ (1.09 g, 4.31mmol), an appropriate amount of $(HOCH_2CH_2)_2S$ (0.53 g, 4.33 mmol) in benzene (60 mL) was added. The reaction mixture was refluxed on a fractionating column for about 6 h. The alcohol in the reaction was fractionated out azeotropically with benzene. Progress as well as the completion of the reaction was checked by the

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†Dedicated to Late Prof. Ram C. Mehrotra

estimation of alcohol in the azeotrope by oxidimetric method[17]. The solvent was removed under vacuum and the product was isolated as white sticky solid. Yield = 98 %. Anal. Found: Ge = 25.5 %, OEt = 31.5 %, S = 11.2 %. Calcd. : Ge = 25.7 %, OEt = 31.8 %, S = 11.3 %. Rest of the members of the series were prepared using the same procedure by adding appropriate amounts of reactants and the details are given in Table-1.

RESULTS AND DISCUSSION

Compounds of the type $GeG_n(OR)_{4-2n}$ have been prepared by the reaction of germanium *tetra*-isopropoxide (or ethoxide) with 2-hydroxyethyl sulphide, 2-mercapto ethyl ether and 2-mercapto ethyl sulphide in different stoichiometric ratios in refluxing anhydrous benzene to yield mono nuclear products of the following types:

$$Ge(OR)_4 + nGH_2 \rightarrow GeG_n(OR)_{4-2n} + 2n\ ROH$$

{where G = $O(CH_2)_2S(CH_2)O$, $S(CH_2)O(CH_2)S$, $S(CH_2)_2S(CH_2)_2S$ and R = Et, Pr^i and n = 1, 2}

All these reactions are quite facile and can be pushed to completion within 5-6 h. The progress of these reactions has been monitored by the estimation of the alcohol present in the benzene-alcohol azeotrope oxidimetrically[17]. These derivatives are white solid/paste and are generally feebly soluble in common organic solvents (like benzene, chloroform, carbon tetrachloride, *etc*). These were purified by washing with dried *n*-hexane. All these derivatives show mononuclear nature in anhydrous boiling benzene. Although complexes 4 and 6 have already been reported[13] still these were re-synthesized *via* a new route for the sake of comparison with other derivatives.

IR spectra: The important bands in IR spectra of the synthesized compounds are in Table-2. Disappearance of ν(OH) at 3400cm^{-1} and ν(SH) at 2550 cm^{-1} in the IR spectra of all the above compounds indicate the formation of Ge-O and Ge-S[18] bands which appear in the region 850-865 cm^{-1} and 420-400 cm^{-1}, respectively. The absence of ν(Ge-S) stretching in the IR spectra of compounds $[(OR)_2Ge\{(OCH_2CH_2)_2S\}]$ and $[Ge\{(OCH_2CH_2)_2S\}_2]$ suggests that the sulphur is not coordinating to germanium atom. Similarly, no band due to ν(Ge-O) has been observed in the IR spectra of $[Ge\{(SCH_2CH_2)_2O\}_2]$ indicating that the oxygen is not linked to the central germanium atom.

^{1}H NMR spectra: Characteristic signals in the ^{1}H NMR spectra of all these derivatives are summarized in Table-3. Disappearance of both OH and SH signals confirms the formation of the compounds. The ^{1}H NMR spectrum exhibit[13] characteristic peaks and peak multiplicities. The signals due to SCH_2 and OCH_2 are observed in the range δ 2.82-δ 3.10 and δ 3.00-δ 3.80 ppm respectively. In the case of 1:1 derivatives,

TABLE-1
SYNTHETIC AND ANALYTICAL DATA FOR Ge(IV) DERIVATIVES OF BIFUNCTIONAL TRIDENTATE LIGAND

S. No	Reactant (g) (a) $Ge(OR)_4$, (b) Ligand	Mol ratio	Complex	ROH (g) Found(Cal.)	Yield (%)	Analysis (% found) Ge	OPr^i	OEt	m.w. Found (Cal.)
1	(a) OEt, 1.09 (b) $(HOCH_2CH_2)_2S$, 0.53	1:1	$(OEt)_2Ge\{(OCH_2CH_2)_2S\}$	0.38 (0.39)	98	25.5 (25.7)	31.5 (31.8)	11.2 (11.3)	270 (283)
2	(a) OEt, 1.00 (b) $(HOCH_2CH_2)_2S$, 0.97	1:2	$Ge\{(OCH_2CH_2)_2S\}_2$	0.72 (0.73)	97	23.0 (23.2)	-	20.3 (20.4)	325 (313)
3	(a) OEt, 1.11 (b) $(HSCH_2CH_2)_2O$, 0.61	1:1	$(OEt)_2Ge\{(SCH_2CH_2)_2O\}$	0.40 (0.41)	98	24.2 (24.3)	29.6 (30.1)	21.3 (21.4)	312 (299)
4	(a) OEt, 1.09 (b) $(HSCH_2CH_2)_2O$, 1.19	1:2	$Ge\{(SCH_2CH_2)_2O\}_2$	0.76 (0.79)	98	20.9 (21.0)	-	37.0 (37.1)	334 (345)
5	(a) OEt, 1.13 (b) $(HSCH_2CH_2)_2S$, 0.69	1:1	$(OEt)_2Ge\{(SCH_2CH_2)_2S\}$	0.40 (0.41)	99	22.9 (23.0)	28.3 (28.6)	30.3 (30.5)	305 (315)
6	(a) OEt, 1.10 (b) $(HSCH_2CH_2)_2S$, 1.34	1:2	$Ge\{(SCH_2CH_2)_2S\}_2$	0.80 (0.80)	98	19.1 (19.2)	-	50.6 (50.9)	352 (377)
7	(a) OPr^i, 1.16 (b) $(HOCH_2CH_2)_2S$, 0.46	1:1	$(OPr^i)_2Ge\{(OCH_2CH_2)_2S\}$	0.44 (0.45)	99	23.1 (23.3)	37.3 (38.0)	10.1 (10.3)	298 (311)
8	(a) OPr^i, 1.10 (b) $(HSCH_2CH_2)_2O$, 0.49	1:1	$(OPr^i)_2Ge\{(SCH_2CH_2)_2O\}$	0.42 (0.43)	97	22.0 (22.2)	35.7 (36.1)	19.3 (19.6)	310 (327)
9	(a) OPr^i, 1.15 (b) $(HSCH_2CH_2)_2S$, 0.58	1:1	$(OPr^{i)}{}_2Ge\{(SCH_2CH_2)_2S\}$	0.43 (0.45)	98	21.0 (21.2)	34.2 (34.4)	27.8 (28.0)	325 (343)

TABLE-2
KEY IR SPECTRAL DATA (cm^{-1}) OF Ge(IV) DERIVATIVES OF BIFUNCTIONAL TRIDENTATE LIGAND

S. No.	Complex	ν(Ge-O)/ν(Ge-S)	Ethoxy/Isopropoxy moiety ν(C-O)	Ligand moiety ν(C-O)/ν(C-S)	ν(C-O-C)/ν(C-S-C)
1	$(OEt)_2Ge\{(OCH_2CH_2)_2S\}$	850 m	1010 m	1080 m	710 m
2	$Ge\{(OCH_2CH_2)_2S\}_2$	860 m	-	1070 m	740 w
3	$(OEt)_2Ge\{(SCH_2CH_2)_2O\}$	415 m	1005 m	640 m	1040 m
4	$Ge\{(SCH_2CH_2)_2O\}_2$	405 m	-	660 m	1025 m
5	$(OEt)_2Ge\{(SCH_2CH_2)_2S\}$	400 m	1015 m	665 m	620 w
6	$Ge\{(SCH_2CH_2)_2S\}_2$	420 m	-	690 m	655 m
7	$(OPr^i)_2Ge\{(OCH_2CH_2)_2S\}$	865 m	1005 m	1080 m	665 m
8	$(OPr^i)_2Ge\{(SCH_2CH_2)_2O\}$	410 w	1000 m	680 m	1030 m
9	$(OPr^i)_2Ge\{(SCH_2CH_2)_2S\}$	400 w	1015 w	660 m	655 m

TABLE-3
^{1}H NMR SPECTRAL DATA (δ ppm) OF Ge(IV) DERIVATIVES

Complex No.	OPr^i/OEt moiety			Ligand Moiety	
	CH_3	CH_2	CH (m)	$-OCH_2$	$-SCH_2$
1	1.18 t	4.32-4.42 q	-	3.08-3.34 m	3.02-3.10 m
2	-	-	-	3.00-3.42 m	2.98-3.07 m
3	1.14 t	4.38-4.46 q	-	3.38-3.62 m	2.82-2.92 m
4	-	-	-	3.42-3.68 m	2.87-2.95 m
5	1.20 t	4.36-4.44 q	-	3.25-3.56 m	2.80-2.90 m
6	-	-	-	3.52-3.60 m	2.85-2.98 m
7	1.26 d	-	4.62-4.96 m	3.05-3.38 m	3.00-3.08 m
8	1.28 d	-	4.46-4.82 m	3.42-3.80 m	2.92-3.05 m
9	1.25 d	-	4.41-4.63 m	-	2.82-2.95 m

TABLE-4
^{13}C NMR SPECTRAL DATA (δ ppm) OF Ge(IV) DERIVATIVES

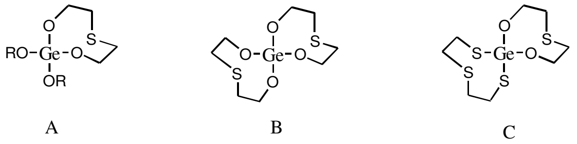
Complex No.	OPr^i/OEt moiety			Ligand Moiety	
	CH_3	CH_2	CH	OCH_2	SCH_2
1	24.82	58.46	-	62.22	33.92
2	-	-	-	60.50	34.68
3	25.16	58.28	-	63.74	32.85
4	-	-	-	64.55	33.22
5	25.12	58.34	-	-	30.42, 32.61
6	-	-	-	-	30.93, 31.58
7	25.82	-	64.12	62.66	34.20
8	25.52	-	64.20	64.93	33.17
9	25.68	-	64.10	-	30.62, 31.81

$-CH_3$, CH_2 and -CH of ethoxy/isopropoxy appear in the ranges of δ1.14-δ 1.28, δ 4.32-δ 4.46 and δ 4.41-δ 4.96 ppm.

^{13}C NMR spectra: The ^{13}C NMR spectra of the above derivatives exhibit[13] $-SCH_2$ and $-OCH_2$ signals in the region δ 30.42-δ 34.68 ppm and δ 60.50-δ 64.93 ppm, respectively, indicate bonding of the ligand moiety to germanium(IV) through S and O of the ligand. Signals of alkoxy carbons (from 1:1 complexes) are also obtained at their expected positions. The ^{13}C NMR spectra of the above synthesized derivatives are given in Table-4.

Conclusion

Based on the molecular weight determinations, IR and NMR (^{1}H and ^{13}C) spectral studies tetra coordinated geometry is more plausible for the above germanium(IV) complexes derived from 2-hydroxyethyl sulfide, 2-mercapto ethyl ether, 2-mercapto ethyl sulfide. Attempts to obtain good quality crystals of these derivatives are in process. It is therefore, difficult to rule out the possibility of coordination of the etheral S/O atom to the central germanium atom in the above derivatives without X-ray crystal structure of at least one product. The probable structures of the synthesized molecules are given as in Fig. 1.



A= $[(OR)_2Ge\{(OCH_2CH_2)_2S\}]$ B= $[Ge\{(OCH_2CH_2)_2S\}_2]$ C=$[Ge\{(SCH_2CH_2)_2S\}_2]$ Where R = Et or Pr^i

Fig. 1. The probable structures of the synthesized molecules

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