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Crystal and molecular structures of (O–Ge)-chelate 1-(dimethylchlorogermylmethyl)pyrrolidone-2 and 1-(dimethylchlorogermylmethyl)piperidone-2, and of (N–Ge)-chelate *O*-(dimethylchlorogermylmethyl)-δ-valerolactim and 2-(chlorodimethylgermylmethylthio)-pyrrolidine-1. Structural correlations between derivatives of four- and five-coordinated germanium

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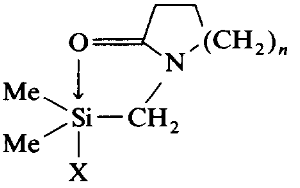
Abstract

An X-ray study of (O–Ge)-chelate 1-(dimethylchlorogermylmethyl)pyrrolidone-2 (**1**), 1-(dimethylchlorogermylmethyl)piperidine-2 (**2**), (N–Ge)-chelate *O*-(dimethylchlorogermylmethyl)-δ-valerolactim (**3**), and 2-(chlorodimethylgermylmethylthio)pyrrolidine-1 (**4**) has been carried out ($R = 0.033$, 0.062, 0.097 and 0.048 for 1241, 2351, 1242 and 1838 reflections, respectively). The Ge atom has a distorted trigonal–bipyramidal [3 + 2] coordination with the axial Cl and O atoms in **1** and **2** or Cl and N atoms in **3** and **4**. The axial distances are Ge–Cl 2.324(2), 2.354(2), 2.458(8) and 2.566(2) Å, Ge ← O 2.311(4) and 2.194(2), Ge ← N 2.148(18) and 2.064(5) Å in **1–4** respectively. Correlation between structural parameters of the compounds of five- and four-coordinated germanium have been considered.

Introduction

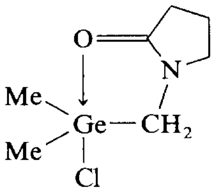
Recently we have carried out X-ray investigation of the following lactam derivatives containing the penta-coordinated Si atom:



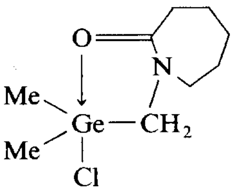
(X = F, Cl, Br, I; $n = 1$–3)

and also of related diacetyl and hydrazine derivatives. This has shown, that along with the preservation of strongly distorted trigonal–bipyramidal coordination of the Si atom, the main geometrical parameters of the coordination centre (axial distances and deviation of the Si atom from the equatorial plane) vary within very wide limits [1]. The estimations of the strength of intramolecular coordinative (hypervalent) O → Si bonding based on X-ray data and IR and NMR-spectroscopy data are in good agreement [2]. The structures of these compounds permit the use of X-ray data for modelling of chemical reaction pathways [3] (in this case, S_N2 reactions) since considerable changes of molecular geometry are observed to take place smoothly in a series of compounds of the same type.

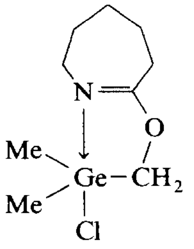
As the next step in our study of coordinative interactions in compounds of the Group IVb elements, using X-ray data to map the S_N2 reaction pathway, we began to study intermediate states of this reaction using structural data on penta-coordinated germanium derivatives. For this purpose we prepared compounds **1**–**4** for X-ray study (for a preliminary report on synthesis and properties of compounds **2** and **3**, see [4]).



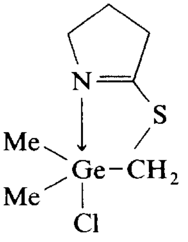
(**1**)



(**2**)



(**3**)



(**4**)

Comparing the (O–Ge)-chelate structures **1** and **2** with the structures, which we have already studied, of analogous (O–Si)-chelate [5] shows that the differences between lengths of equatorial Si–C and Ge–C bonds are close to the differences between the covalent radii of Si and Ge (0.06 Å), whereas the differences of the corresponding axial bond lengths are considerably larger (in particular, Si ← O 1.95 Å, but Ge ← O 2.31 Å in **1** and 2.19 Å in **2**, that is 0.24–0.36 Å). The increase of "geometrical" electronegativity of the central atom from 1.7(Si) to 2.1(Ge) [6] is therefore to be expected.

Results of X-ray investigation

The crystal structural data for compounds **1**–**4** are presented in Table 1. Unit cell parameters and reflection intensities were measured at $-120\,^{\circ}\mathrm{C}$ with a four-circle automatic "Syntex $P2_1$" diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scan). All the structures were solved by the direct method and refined anisotropically by block-diagonal least-squares for non-hydrogen atoms. H atoms in structures **1**–**4** were located in the difference syntheses; in structures **1**, **2** and **4** they were refined isotropically, in the structure **3** were included in calculation of structural factors with $B_{iso} = 4$ Å^2 without refinement. Calculations for the structures **1**–**3** were carried out with an Eclipse S/200 computer using the INEXTL program [7]; calculations for structure **4** were made with a IBM personal computer

Table 1

Crystal and structural data for compounds **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_7H_{14}NOGeCl$	$C_9H_{18}NOGeCl$	$C_9H_{18}NOGeCl$	$C_7H_{14}NSGeCl$
a (Å)	9.212(3)	6.259(1)	8.357(3)	13.341(3)
b	9.514(3)	9.022(2)	12.575(3)	12.643(3)
c	11.269(3)	11.489(3)	11.680(4)	12.282(2)
α (°)	90	70.64(2)	90	90
β	90	86.12(2)	104.79	90
γ	90	86.67(2)	90	90
V (Å^3)	987.6	610.2	1192.5	2071.6(8)
Z	4	2	4	8
d_{calc} (Mg/m^3)	1.589	1.438	1.472	1.618
Space group	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$	$Pbca$
$2\theta_{max}$ (°)	54.0	60.0	45.0	55.0
Number of reflections with $I > 6\sigma(F)$	1241	2351	1242	1838
R	0.033	0.062	0.097	0.048
R_w	0.037	0.063	0.137	0.042

Table 2

Atomic coordinates ($\times 10^5$ for Ge, $\times 10^4$ for Cl, O, N, C and $\times 10^3$ for H) and equivalent isotropic (isotropic for H atoms) temperature parameters B(Å^2) in structure **1**

Atom	x	y	z	B
Ge	4076(7)	76936(7)	87254(6)	1.33(1)
Cl	926(2)	8711(2)	10551(1)	1.89(4)
O	−894(5)	6930(5)	6893(4)	2.3(1)
N	−2166(6)	8366(6)	7389(5)	1.5(1)
C(1)	147(7)	5762(7)	9277(6)	1.8(2)
C(2)	2212(7)	8195(8)	7951(6)	2.5(2)
C(3)	−1385(6)	8818(6)	8540(5)	1.4(1)
C(4)	−3585(7)	8909(8)	7141(6)	2.2(2)
C(5)	−4021(7)	7888(8)	6160(7)	2.9(2)
C(6)	−2602(7)	7271(8)	5695(6)	2.6(2)
C(7)	−1585(7)	7466(7)	6738(5)	1.8(1)
H(1.1)	69(7)	534(7)	963(6)	7(2)
H(1.2)	−61(7)	570(7)	971(5)	5(2)
H(1.3)	2(8)	508(7)	864(6)	6(2)
H(2.1)	313(7)	800(7)	838(5)	6(2)
H(2.2)	244(7)	777(7)	717(5)	2(2)
H(2.3)	233(7)	902(6)	782(5)	3(1)
H(3.1)	−112(6)	975(5)	859(5)	3(1)
H(3.2)	−221(6)	878(6)	925(5)	0(1)
H(4.1)	−363(7)	1021(7)	681(6)	3(2)
H(4.2)	−430(7)	892(7)	779(5)	8(2)
H(5.1)	−496(7)	830(7)	515(5)	3(2)
H(5.2)	−477(6)	704(6)	665(5)	12(2)
H(6.1)	−165(9)	805(10)	532(8)	9(3)
H(6.2)	−271(9)	652(9)	602(7)	9(3)

Table 3

Atomic coordinates ($\times 10^4$ for Ge, Cl, O, N and $\times 10^3$ for C and H) and equivalent isotropic (isotropic for H atoms) temperature parameters B(Å^2) in structure **2**

Atom	*x*	*y*	*z*	*B*
Ge	855(1)	−662(1)	7425(1)	3.88(2)
Cl	1325(3)	1908(2)	6053(2)	5.90(7)
O	732(8)	−3180(5)	8476(5)	5.8(2)
N	2869(8)	−3273(6)	6882(5)	4.1(2)
C(1)	210(1)	−33(1)	879(1)	6.1(3)
C(2)	−226(1)	−66(1)	740(1)	7.3(3)
C(3)	262(1)	−153(1)	629(1)	5.3(2)
C(4)	421(1)	−412(1)	618(1)	5.0(3)
C(5)	619(1)	−490(1)	684(1)	6.0(3)
C(6)	585(1)	−643(1)	782(1)	6.1(3)
C(7)	432(1)	−633(1)	888(1)	6.1(3)
C(8)	204(1)	−572(1)	851(1)	5.3(3)
C(9)	184(1)	−398(1)	793(1)	4.3(2)
H(4.1)	449(9)	−327(6)	540(5)	5(2)
H(4.2)	327(9)	−488(7)	618(5)	5(2)
H(5.1)	722(10)	−422(7)	731(6)	8(2)
H(5.2)	727(17)	−511(12)	647(10)	20(4)
H(6.1)	729(11)	−676(7)	792(6)	9(2)
H(7.1)	494(10)	−614(7)	947(6)	8(2)
H(8.2)	140(11)	−635(7)	786(6)	7(2)
H(1.1)	169(11)	−104(7)	938(6)	10(2)
H(1.2)	175(10)	40(7)	871(5)	8(2)
H(2.1)	−271(9)	−124(6)	781(5)	5(2)
H(3.1)	185(8)	−119(5)	532(5)	5(1)
H(3.2)	249(9)	−150(6)	622(5)	5(2)
H(6.2)	542(9)	−733(6)	754(5)	5(1)
H(7.2)	428(10)	−735(7)	963(6)	9(2)
H(8.1)	135(10)	−611(7)	956(6)	7(2)
H(1.3)	371(10)	−43(7)	874(6)	9(2)
H(2.2)	−272(11)	−74(8)	656(6)	10(2)
H(2.3)	−292(13)	21(9)	775(7)	16(2)

Table 4

Atomic coordinates ($\times 10^3$ for O, N, C and $\times 10^4$ for Ge, Cl, $\times 10^2$ for H) and equivalent isotropic (isotropic for H atoms) temperature parameters B(Å^2) in structure **3**

Atom	*x*	*y*	*z*	*B*
Ge	4931(3)	2841(2)	647(2)	1.81(7)
Cl	2039(8)	2461(6)	−356(7)	4.3(2)
O	546(2)	407(1)	280(1)	2.7(5)
N	717(2)	342(1)	182(2)	1.8(6)
C(1)	523(3)	355(2)	−78(2)	3.6(9)
C(2)	550(3)	127(2)	77(4)	7(2)
C(3)	418(3)	367(2)	186(2)	2.5(8)
C(4)	696(3)	397(2)	267(2)	2.1(8)
C(5)	825(3)	446(2)	360(2)	2.4(8)
C(6)	910(3)	533(2)	307(2)	3.7(9)
C(7)	1031(3)	503(2)	236(3)	4(1)
C(8)	956(3)	436(2)	129(3)	3.5(9)
C(9)	884(3)	333(3)	165(3)	6(1)

Table 5

Atomic coordinates ($\times 10^4$ Ge, Cl, S, N, C and $\times 10^3$ for H) and equivalent isotropic (isotropic for H) temperature parameters B(Å^2) in structure **4**

Atom	x	y	z	B
Ge	7049(1)	4898(1)	1516(1)	19(1)
Cl	5432(1)	5905(1)	1970(1)	28(1)
S	6970(1)	3579(1)	−677(1)	25(1)
N	8222(4)	4005(4)	918(4)	19(2)
C(1)	6962(6)	4122(5)	2860(6)	29(2)
C(2)	7776(5)	6195(6)	1377(7)	28(3)
C(3)	6270(5)	4396(6)	270(6)	30(2)
C(4)	8094(5)	3514(5)	41(5)	22(2)
C(5)	8982(5)	2887(5)	−373(5)	27(2)
C(6)	9805(5)	3397(6)	334(7)	36(3)
C(7)	9251(5)	3806(6)	1330(6)	28(2)
H(1.1)	6726(5)	3343(5)	2774(5)	46(2)
H(1.2)	6560(4)	4525(5)	3298(5)	32(2)
H(1.3)	7555(5)	3948(5)	3151(5)	37(2)
H(2.1)	7429(5)	6600(5)	1860(5)	59(3)
H(2.2)	7659(5)	6432(5)	452(5)	43(2)
H(2.3)	8231(4)	6105(4)	1560(5)	0(2)
H(3.1)	5828(5)	4021(5)	538(5)	35(2)
H(3.2)	5999(5)	5250(4)	−46(5)	63(2)
H(5.1)	9013(5)	2923(5)	−1214(5)	40(2)
H(5.2)	8723(5)	1926(5)	−30(5)	44(2)
H(6.1)	10206(5)	2999(5)	546(5)	32(2)
H(6.2)	10316(6)	4036(6)	−296(6)	108(3)
H(7.1)	9225(4)	3376(4)	1950(4)	27(2)
H(7.2)	9626(3)	4690(3)	1582(3)	0(1)

Table 6

Bond lengths (Å) in structures **1**–**4**

Bond	**1**	**2**	**3**	**4**
Ge–Cl	2.324(2)	2.354(2)	2.458(8)	2.566(2)
Ge–C(1)	1.955(7)	1.915(8)	1.965(27)	1.925(7)
Ge–C(2)	1.938(7)	1.951(7)	2.027(28)	1.913(8)
Ge–C(3)	1.979(6)	1.979(7)	1.981(24)	1.955(7)
Ge ← O	2.311(4)	2.194(5)	–	–
Ge ← N	–	–	2.148(18)	2.064(5)
C(3)–N	1.451(8)	1.496(9)	–	–
C(3)–O	–	–	1.423(29)	–
C(3)–S	–	–	–	1.814(8)
S–C(7)	–	–	–	1.741(6)
O–C(7)	1.223(8)	–	–	–
N–C(7)	1.318(8)	–	–	1.255(8)
O–C(9)	–	1.258(8)	1.317(28)	–
N–C(9)	–	1.300(8)	1.260(29)	–
N–C(4)	1.460(8)	1.474(9)	1.473(33)	1.485(8)
C(4)–C(5)	1.526(10)	1.512(11)	1.565(40)	1.521(11)
C(5)–C(6)	1.527(10)	1.477(12)	1.479(41)	1.541(10)
C(6)–C(7)	1.514(9)	1.515(11)	1.520(40)	1.514(9)
C(7)–C(8)	–	1.536(11)	1.519(35)	–
C(8)–C(9)	–	1.493(1)	1.459(33)	–

Table 7

Bond angles (°) in structures **1**–**4**

Angle	**1**	**2**	**3**	**4**
ClGeO	171.3(1)	170.6(2)	–	–
ClGeN	–	–	164.9(5)	170.3(1)
ClGeC(1)	97.8(2)	95.6(3)	90.5(8)	90.9(2)
ClGeC(2)	96.8(2)	97.5(3)	91.7(9)	91.2(2)
ClGeC(3)	92.3(2)	90.4(2)	89.3(7)	83.4(2)
C(1)GeC(2)	118.7(3)	118.9(4)	115(1)	123.0(3)
C(1)GeC(3)	116.1(3)	120.7(3)	120(1)	118.3(3)
C(2)GeC(3)	112.4(3)	118.5(3)	125(1)	118.8(3)
OGeC(1)	87.1(2)	89.4(3)	–	–
OGeC(2)	87.1(2)	86.9(3)	–	–
OGeC(3)	79.0(2)	80.2(3)	–	–
NGeC(1)	–	–	96.3(9)	94.1(3)
NGeC(2)	–	–	98(1)	93.0(3)
NGeC(3)	–	–	75.6(9)	86.9(2)
GeC(3)N	109.8(4)	108.7(4)	–	–
GeC(3)O	–	–	115(2)	–
GeC(3)S	–	–	–	114.4(4)
GeNC(9)	–	–	115(2)	–
GeOC(9)	–	110.7(4)	–	–
GeNC(7)	–	–	–	118.2(4)
GeOC(7)	106.4(4)	–	–	–
GeNC(4)	–	–	127(2)	132.2(4)
C(3)NC(9)	–	120.3(6)	–	–
C(3)OC(9)	–	–	115(2)	–
C(3)NC(7)	121.0(5)	–	–	–
C(3)SC(7)	–	–	–	98.4(3)
NC(9)O	–	120.0(6)	118(2)	–
NC(7)O	123.0(6)	–	–	–
SC(7)N	–	–	–	121.9(5)
NC(4)C(5)	101.8(5)	112.7(6)	115(2)	103.4(5)
C(4)C(5)C(6)	105.5(6)	115.0(7)	110(2)	104.5(5)
C(5)C(6)C(7)	102.5(5)	114.4(7)	113(2)	98.6(5)
C(6)C(7)N	109.1(5)	–	–	116.1(5)
C(6)C(7)S	–	–	–	121.9(5)
C(6)C(7)C(8)	–	114.9(7)	119(2)	–
C(7)C(8)C(9)	–	113.6(6)	110(2)	–
C(8)C(9)N	–	120.7(6)	127(2)	–
C(8)C(9)O	–	–	115(2)	–
C(9)NC(4)	–	123.0(6)	118(2)	–
C(7)NC(4)	114.9(5)	–	–	109.6(5)

Table 8

Puckering parameters of lactam cycles [25]

Compound	*M*	*Q* (Å)	ϕ (°)
1	2	0.2444	254.0050
2	2	0.4343	51.0403
	3	0.6362	76.5847
3	2	0.4462	120.4525
	3	0.6438	104.1858
4	2	0.2777	290.1459

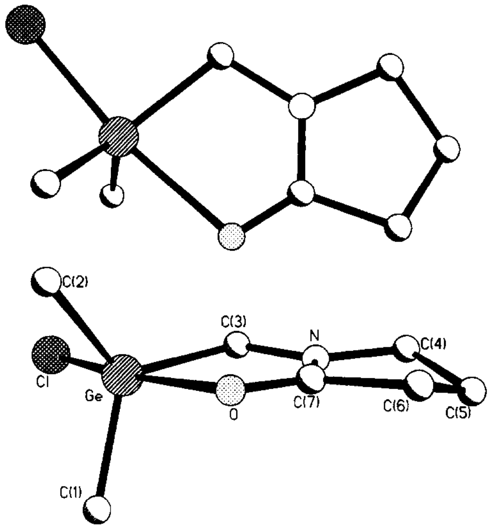


Fig. 1. Structure of molecule **1**.

using the SHELXTL PLUS programs. The general view of molecules **1–4** with atom numbering is given in Figs. 1–4. The atomic coordinaties and temperature factors are given in Tables 2–5, bond lengths and angles in Tables 6 and 7.

The Ge atom in structures **1–4** has a distorted five-fold trigonal–bipyramidal coordination with the C(1),C(2),C(3) atoms in equatorial and the O (or N) and Cl atoms in axial positions. Five-membered chelate cycles formed by the coordinative Ge ← O (or Ge ← N) bond have an envelope conformation with the Ge atom deviating by 0.22 Å in **1**, 0.10 Å in **2** and 0.08 Å in **3** and **4**. The seven-membered

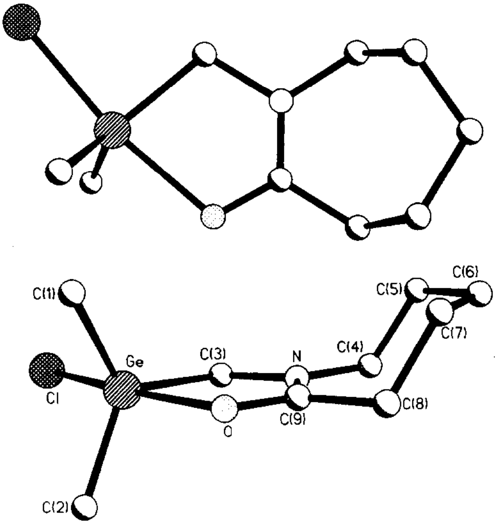


Fig. 2. Structure of molecule **2**.

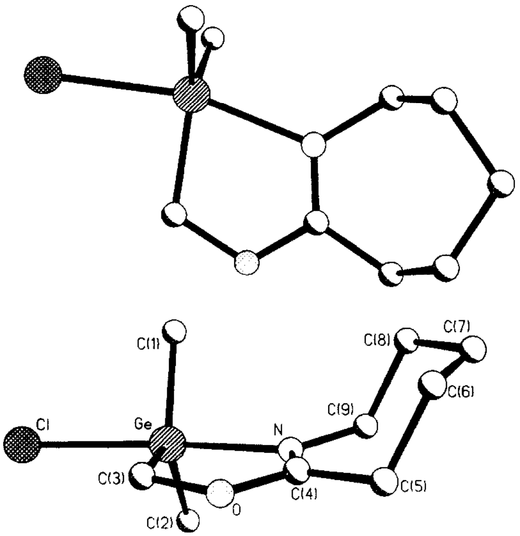


Fig. 3. Structure of molecule **3**.

N-heterocylces in **2** and **3** have a chair conformation, the five-membered *N*-heterocycles in **1** and **4** have an envelope conformation with a deviation of one atom from the plane of four others (in **1** C(5) by 0.36 Å, in **4** C(6) by 0.44 Å). Conformation parameters [25] of *N*-heterocycles are given in Table 8.

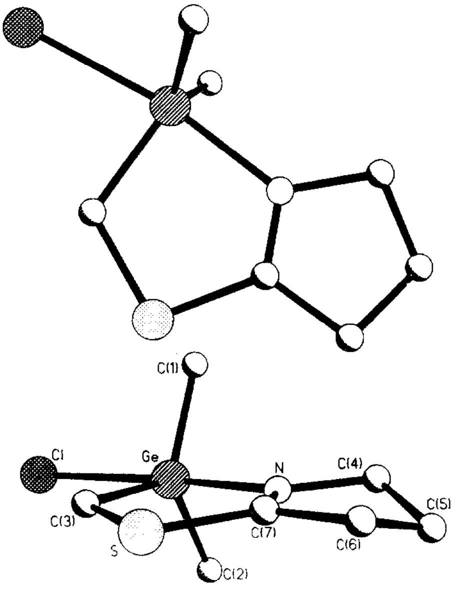


Fig. 4. Structure of molecule **4**.

Structural correlations

The principle of the method of structural correlations has been formulated by Burgi [8] and Dunitz [9] who applied it to structures of trigonal-bipyramidal complexes with Cd and Sn central atoms. In particular the relation of axial bond lengthening (Δx, Δy) and the deviation of a central atom from the equatorial plane (Δz) has been discussed. Dependence equations are considered as showing the change in complex geometry in the course of S_N2 nucleophilic substitution at the central atom. Structural features of the molecules **1**–**4**, as well as of some other derivatives of penta-coordinated Ge with the axial X–Ge ← Y moiety (X = Cl, Y = O or N) are essential for such treatment and are repeated in Table 9 (Cambridge Structural Database [10]). Structural formulas of these compounds are given in Fig. 9. In the present paper two types of molecules are considered: with three equatorial carbon atoms (series C_3, index $m = 1$) and with two equatorial chlorine atoms and one equatorial carbon atom (series Cl_2C, $m = 2$). By plotting the points

Table 9

Comparison of axial distances $x_m = d$(Ge–X) and $y_m = d$(Ge–Y), deviation z_m of the Ge atom from the equatorial plane, increment bond orders n_x and n_y, and total hypervalent bond orders (x_m^0, y_m^0, z_m^{max} are parameters observed in corresponding "standard" structures)

Struct.	Atom		Distance			Increment bond order		Total bond order	
	X	Y	x_m	y_m	z_m	n_x	n_y	$n_x + n_y$	$n'_x + n'_y$
Series C_3 (m = 1) [a]									
a	Cl	–	2.17	–	0.52	1.000	0.000	1.000	
5 [a]	Cl	N	2.301	2.508	–	0.718	0.229	0.947	–
5' [b]	Cl	N	2.327	2.479	–	0.672	0.246	0.919	–
1	Cl	O	2.324	2.311	0.192	0.677	0.320	0.997	–
2	Cl	O	2.354	2.194	0.154	0.628	0.430	1.058	–
3	Cl	N	2.458	2.148	0.003	0.483	0.569	1.052	–
4	Cl	N	2.566	2.064	−0.048	0.367	0.704	1.071	–
Series Cl_2C (m = 2) [a]									
b	Cl	–	2.13	–	0.58	1.000	0.000	1.000	1.000
6	Cl	O	2.134	3.228	0.577	0.990	0.024	1.014	1.022
7	Cl	O	2.140	3.075	0.533	0.975	0.035	1.010	1.019
8	Cl	O	2.160	2.790	0.520	0.927	0.072	0.999	1.008
9	Cl	O	2.169	2.770	0.476	0.906	0.076	0.982	0.991
10	Cl	O	2.181	2.507	0.428	0.879	0.147	1.026	1.033
11	Cl	O	2.253	2.166	0.223	0.733	0.349	1.082	1.080
12	Cl	O	2.253	2.140	0.190	0.733	0.373	1.106	1.102
13	Cl	O	2.264	2.123	0.201	0.713	0.383	1.096	0.098
14	Cl	O	2.239	2.092	0.200	0.759	0.383	1.142	1.173
14' [b]	Cl	O	2.252	2.080	0.175	0.735	0.359	1.094	1.161

[a] $m = 1$ corresponds to the equatorial plane C_3 in the structures (1)–(4) [this work] and (5) [22], $m = 2$ corresponds to the plane Cl_2C in the structures (6),(7),(9)-(13) [16], (8) [23] and (14) [24]. $z^{max} = 0.52$ and $z^{max} = 0.58$ A are calculated for molecules (a) [11] and (b) [12]. [b] The crystal is built of two symmetrically independent molecules. [c] Only the bond distances and some angles in structure **5** are published.

$\Delta_m x = f(z_m)$ and $\Delta_m y = f(-z_m)$, we obtain a relationship (Fig. 5) which is described by Burgi's logarithmic equation [8]:

$$\Delta_m x = -c \lg\left[\left(z_m^{\max} + z_m\right)/2z_m^{\max}\right] \tag{1}$$

$$\Delta_m y = -c \lg\left[\left(z_m^{\max} - z_m\right)/2z_m^{\max}\right] \tag{1}$$

where c is a constant, and where $\Delta_m x = x_m - x_m^0$ and $\Delta_m y = y_m - y_m^0$ are increments or differences of Ge–X (x_m) and Ge ← Y (y_m) axial distances from their standard values (x_m^0 and y_m^0); z_m is the deviation of Ge atom from equatorial plane towards the axial X substituent, $z_m^{\max}$ is the z_m value for tetrahedral coordination, when $\Delta_m y = \infty$.

The standard values x_m^0, y_m^0 and $z_m^{\max}$ are taken from structural data on compounds of four-coordinated Ge within its environment, which of course apart from the second axial ligand coincides with the environment in the derivatives of

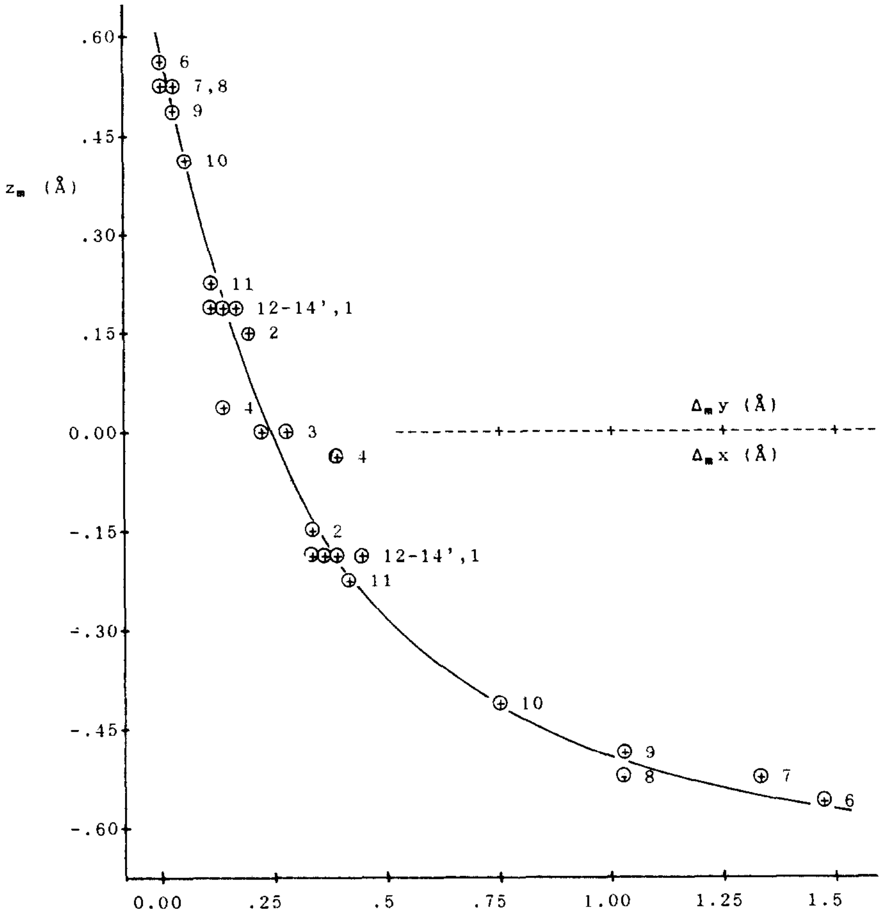
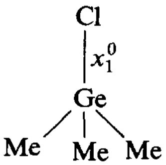
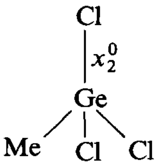


Fig. 5. Plot of the distance increments $\Delta_m y$ and $\Delta_m x$ as a single function of z_m. Points are numbered according to the codes given in Fig. 9.

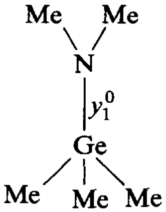
five-coordinated Ge which are under consideration. The following molecules should be considered as closest to the compounds:



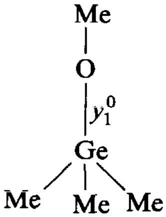
(a)



(b)



(c)



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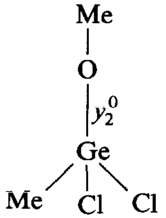


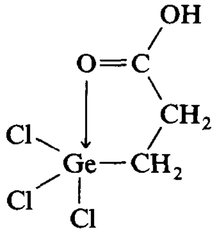
(e)

Structures of molecules **a** [11] and **b** [12] have been determined by electron diffraction and microwave spectroscopy. Structural data on compounds **c**, **d** and **e** are not to be found in the literature and therefore values for y_1^0 and y_2^0 were taken from the structures of similar larger molecules: (**c**′) $Me_3GeN(Me)CH_2(S)$-$CH_2(S)N(Me)GeMe_3$ [13], (**d**′) $Ph_3GeOC(O)CF_3$ [14], (**e**′) $Hg_2[GeO_4]$ [15,16].

In accordance with eq. 1 the relation of $\Delta_m x$ and $\Delta_m y$ vs. $\lg[(z_m^{\max} \pm z_m)/2z_m^{\max}]$ is linear (Fig. 6). Treatment of this dependence by least squares reduces it to eq. 1′:

$$\Delta_m x,\ \Delta_m y = -0.687 \lg\left[\left(z_m^{\max} \pm z_m\right)/2z_m^{\max}\right] \qquad (1')$$

with correlation coefficient $r = -0.958$ and standard error 0.0495. In Fig. 6, the point on the graph representing structure **6** is not located on the straight line drawn through the other points. This compound has the highest value of $\Delta_2 y$, 1.478 Å, i.e. its coordination Ge ← O is weakest. In this structure the Ge atom deviates from the equatorial plane z_2, but this deviation and the axial Ge–Cl bond length x_2 observed are within the accuracy limits of the corresponding standard values noted in the four-coordinated compound. It seems that the coordinative interaction Ge–O in structure **6** may be considered as a purely electrostatic attraction, rather than a hypervalent interaction due to formation of a three-centre four-electron bond [17]. The coordinative Ge ← O interaction in structure **6** may arise from the influence of the OH^- group involved in the –O–H ··· O= hydrogen bond which links molecules **6** into dimers [18]. If the point representing structure **6** in Fig. 6 is ignored the general equation of dependence becomes (eq. 1″)



(6)

$$\Delta_m x,\ \Delta_m y = -0.911 \lg\left[\left(z_m^{\max} \pm z_m\right)/2z_m^{\max}\right] \qquad (1'')$$

with a much better correlation coefficient $r = -0.992$ and standard error 0.029. The above value of constant c will be used below.

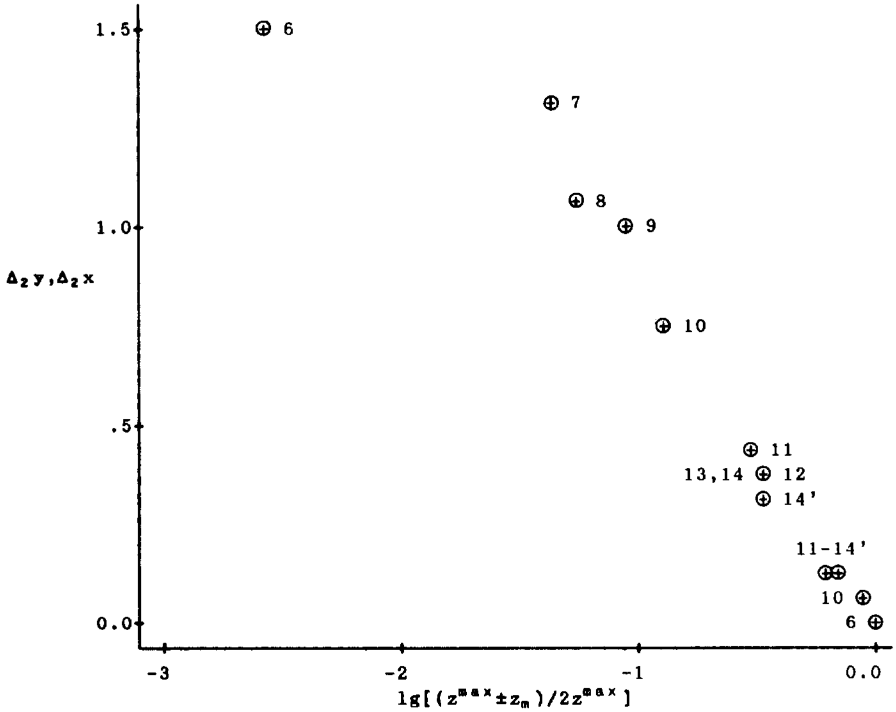


Fig. 6. Plot of $\Delta_2 x$, $\Delta_2 y$ vs. $\lg[(z_2^{\max} \pm z_2)/2z_2^{\max}]$.

Previous workers [9] assumed the total order of the central Ge atom is constant and equal to 4 both by four-fold tetrahedral and by five-fold trigonal–bipyramidal coordination. If it is supposed that on going from tetrahedral to trigonal–bipyramidal coordination the equatorial bonds usually remain covalent the order of each such bond is taken as 1. Then taking into account the Pauling's logarithmic relationship between bond distance and bond order [19]

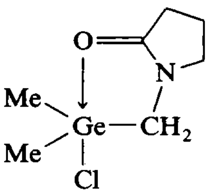
$$\Delta_m x = x_m - x_m^0 = -c \lg(n_x) \quad \text{and} \quad \Delta_m y = y_m - y_m^0 = -c \lg(n_y)$$

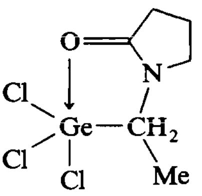
where n_x and n_y are orders of hypervalent bond components Ge–Y and Ge–X and c is a constant, the total hypervalent bond order equation and increments of axial distances are related thus:

$$n_x + n_y = 10^{-\Delta_m x/c} + 10^{-\Delta_m y/c} = 1 \qquad (2)$$

If constant c takes the value 0.91, according to eq. 1″, it is easy to check the assumption about preservation of the sum $N = 1$ of hypervalent bond components (eq. 2). The N values are given in Table 9 from which it can be seen that in reality N is not constant and starting with the structure **2**, in the series C_3 and with the structure **11** in the series Cl_2C the value of N exceeds 1 appreciably. On going from **10** to **11** the distance corresponding to Ge ← O coordinative interaction drops sharply by 0.34 Å and the Ge–Cl bond distances increase by 0.07 Å. Thus structures of the series Cl_2C may be divided into two subgroups: **6–10** with a "weaker" Ge ← O coordinative interaction and **11–14** with a "stronger" interaction (Table 9). Molecules in the subgroups differ from each other only by the presence of an electron donor (in this case, N atom) in the environment of the hypervalent fragment. This is apparently the reason for a sharp shortening of distances in the axial moiety on going from the first to the second subgroup.

To make a similar S_N2 division in the series C_3 it is necessary to take into account that a considerable decrease of electronegativity of the equatorial substituents causes lengthening of both components of the hypervalent bond, which is often considered equivalent to their weakening (cf., e.g., [20]). For structures with the axial moiety O–Ge–Cl this lengthening is obvious from comparison of the structures **1** and **12**:


(1)


(12)

From Table 9 it can be seen that correction (shortening) of the Ge ← O bond on going from the series C_3 to the series Cl_2C equals 0.17 Å and for the Ge–Cl bond 0.07 Å with increasing of the standard value from $z_1^{max} = 0.52$ to $z_2^{max} = 0.58$ Å. Taking this shortening into account it is possible to assign structures **1** and **2** to the subgroup with a "stronger" coordinative Ge ← O interaction. The values of hypervalent bond orders in the series C_3 determined by using $c = 0.91$ are given for comparision.

Correction values for the influence of the equatorial environment cannot be estimated for the structures (**3–5**) where there is a coordinative Ge ← N interaction, but **3** and **4** involve a strong interaction, while that in **5** is weaker. This conclusion is reached by analogy with the series Cl_2C, by taking into account the great difference between total order values of N → Ge–Cl hypervalent bonds in **5** and in **3** and **4**. Also there are qualitative differences in the molecules. In **5** the hypervalent moiety is surrounded by a purely hydrocarbon skeleton, whereas in **3** and **4** this skeleton contains one O and one S atom, respectively.

For both Cl_2C and C_3 series a "weaker" interaction Ge ← Y (*O*, *N*) takes place at the distances 3.23–2.48 Å with the Ge–X (*Cl*) distances 2.13–2.33 Å; the corresponding values for "stronger" interactions are Ge ← Y 2.31–2.06 Å and Ge–X (*Cl*) 2.24–2.57 Å. The areas with "weaker" and "stronger" interactions as well as structures with the Ge ← N coordination are distinguishable in Fig. 5. Bond distance increments of the hypervalent moiety for a "stronger" Ge ← Y interaction are confined within a rather narrow interval.

The clustering algorithm may be used to separate "stronger" and "weaker" interaction areas [21] (Fig. 7).

The electron-donating ability of the N atom influences the total hypervalent bond order which in structures **1–4** and **11–14** noticeably exceeds 1. This is revealed

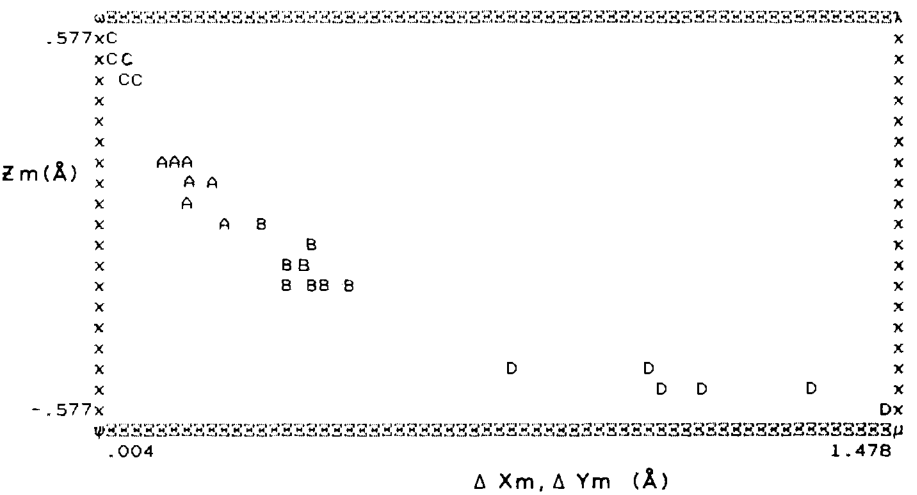


Fig. 7. Plot of the distribution of the distance increments $\Delta_m y$ and $\Delta_m x$ by the clustering algorithm (A = cluster 1, B = cluster 2, C = cluster 3, etc.)

by refinement of standard bond distances x_m^0 and y_m^0. Indeed using the following relations (eq. 1)

$$x_m^0 = x_m + c \lg\left[\left(z_m^{\max} + z_m\right)/2z_m^{\max}\right]$$

$$y_m^0 = y_m + c \lg\left[\left(z_m^{\max} - z_m\right)/2z_m^{\max}\right]$$

the standard bond distances x_m^0 and y_m^0 in an axial moiety may be estimated for the corresponding equatorial environment. Unfortunately, the values x_1^0 and y_1^0 for the series C_3 cannot be determined because of the insufficient number of experimental points.

In Fig. 8 plots of dependence x_2 and y_2 distances on $\lg[(z_2^{\max} \pm z_2)/2z_2^{\max}]$ for a "weaker" interaction in the series Cl_2C are given, which are approximated by the least squares equations:

$$x_2 = -0.817 \lg\left[(0.58 + z_2)/2 \times 0.58\right] + 2.133 \quad (r = -0.921)$$

$$y_2 = -0.922 \lg\left[(0.58 - z_2)/2 \times 0.58\right] + 1.724 \quad (r = -0.915)$$

The calculated values $x_2^0 = 2.13$ Å and $y_2^0 = 1.72$ are sufficiently close to those observed in structurally similar compounds of four-coordinated germanium, namely Ge–Cl 2.13 Å (**b**′) and Ge ← O 1.75 Å (**e**′). An analogous relationship for structures with a "stronger" coordinative Ge–Y interaction is not observed (the correlation coefficients are $r = 0.04$ for x_2 and $r = -0.76$ for y_2), which is probably due to a great repulsion of axial ligands from the equatorial moiety at shorter Ge–Y distances.

A similar calculation for the series Cl_2C with the refined standard values $x_2^0 = 2.13$ and $y_2^0 = 1.72$ Å (with the new value $c = 0.93$) shows a greater difference in total hypervalent bond order between the structures with "weaker" and "stronger" interactions. The refined values of total bond order $(n_x' + n_y')$ are given in the last column of Table 9.

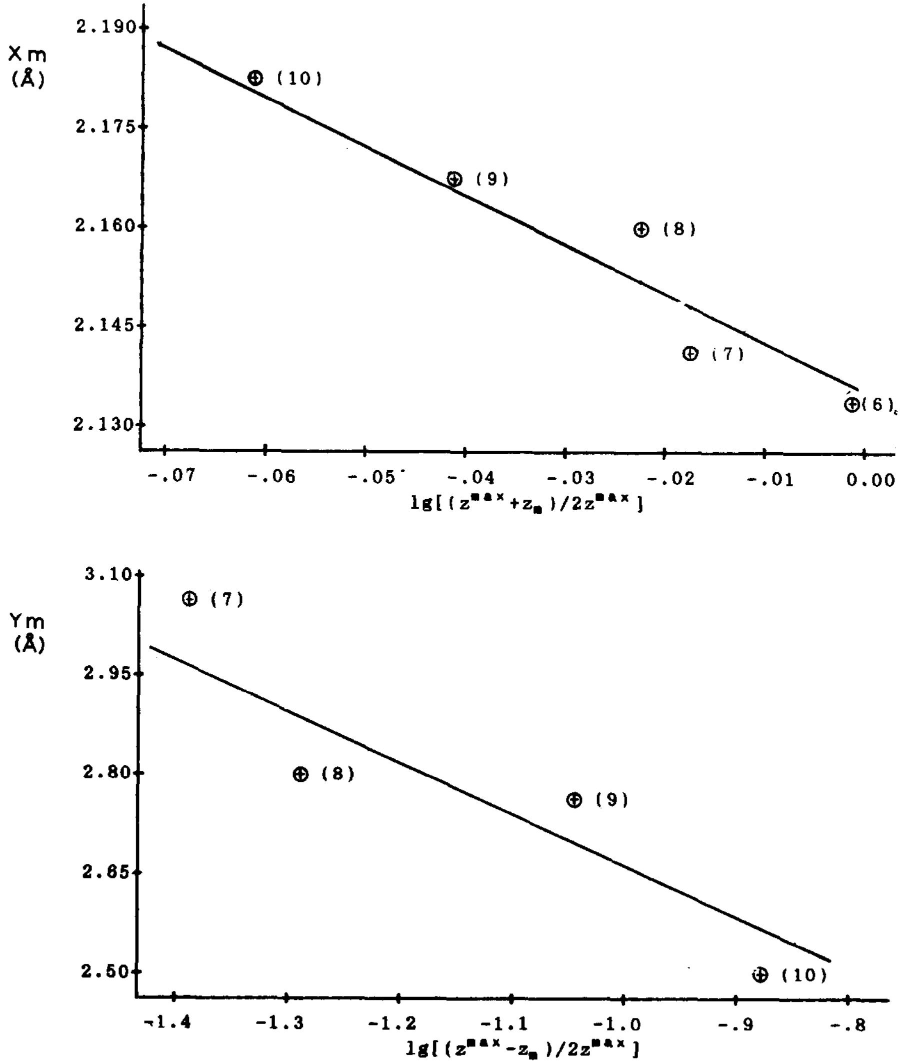
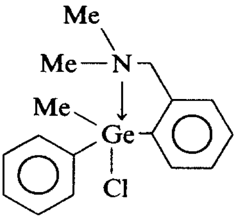


Fig. 8. Determination of the standard values of the distances x_2^0 (a) and y_2^0 (b) in structures with a weak interaction Ge ← O.

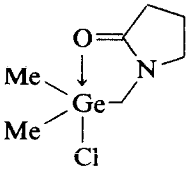
On the basis of the above calculation and revision of the standard bond distances one can conclude that a violation of the relation 2 is caused by reinforcement of a coordinative interaction due to the presence of an electrondonating atom (in this case, N or S) in the molecular skeleton surrounding the hypervalent moiety.

Thus, through using data on the geometry of penta-coordinated Ge atom in 4 compounds, whose X-ray study is reported in this work, and on 11 structures taken from the literature, the correlations between the main structural parameters in derivatives of four- and five-coordinated Ge atom have been found.

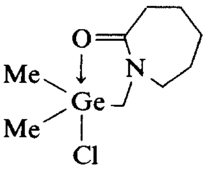
Series C_3



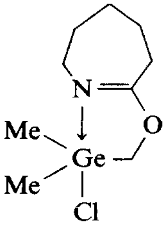
(5)



(1)



(2)



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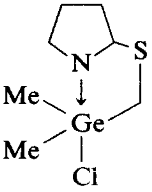
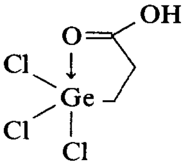
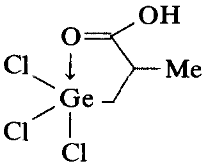


(4)

Series Cl_2C



(6)



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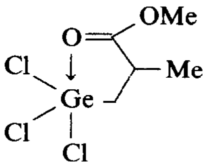
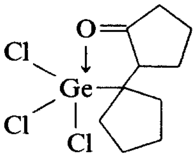
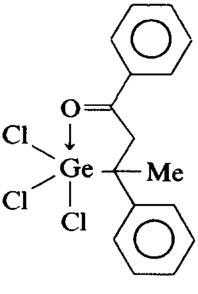


(8)



(9)



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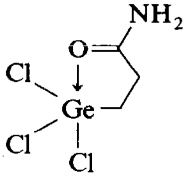

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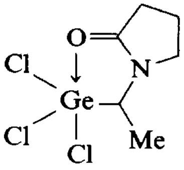

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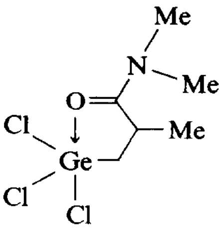

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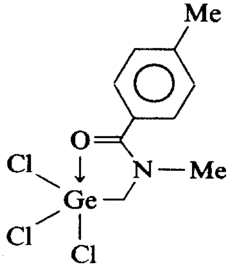

(14)

Fig. 9. Structure formulas of the discussed compounds.

Experimental

1-(Dimethylchlorogermylmethyl)pyrrolidone-2 (**1**) was prepared by interaction (4.7 g, 0.025 *M*) of dimethylchloromethylchlorogermane with 4 g (0.0254 *M*) of 1-trimethylsilylpyrrolidone-2 on heating (120–130 °C) and distilling of Me_3SiCl. By fractionation 5 g (84%) of compounds **1** was obtained. M.p. 52–55 °C. Found: C, 35.70; H, 5.86; N, 6.31; Ge, 30.95; Cl, 14.50. $C_4H_{14}NOGeCl$ calc: C, 35.59; H, 5.97; N, 5.95; Ge, 30.69; Cl, 15.03%.

Preparation of compounds **2** and **3** is reported in the preliminary communication [4].

*2-(Chlorodimethylgermylmethylthio)pyrrolidine-1 (**4**).* *N*-trimethylgermylpyrrolidinethione-2 (0.5 g, 0.0029 *M*) and dimethylchloromethylchlorogermane (1 g, 0.0053 *M*) were mixed by magnetic stirrer 1 h in vacuo at 70 °C. After removal of low-boiling substances in vacuo white crystalline powder was obtained. The yield of **4** was 1.08 g (100%). M.p. 84–85 °C. Found: C, 33.37; H, 6.11; Cl, 13.82; Ge, 27.57; N, 5.51; S, 12.48. $C_7H_{14}NSGeCl$ calc: C, 33.3; H, 5.55; Cl 14.1; Ge, 28.8; N, 5.55; S, 12.7%. IR-spectrum (in $CHCl_3$): ν(C=N) 1600 cm^{-1}.

Acknowledgements

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