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Interaction of the (O → Ge)-chelate bis-(lactamo-*N*-methyl)-*cis*-dichlorogermanes with trimethylsilyltriflate. Synthesis of bis-(lactamo-*N*-methyl)-*trans*-(trifluoromethylsulfonyloxy)chlorogermanes

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Abstract

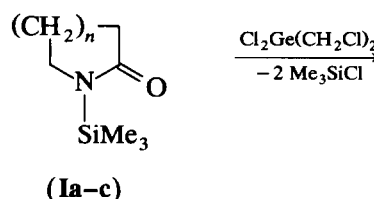
Regardless of the ratio of reagents, the interaction of the (O → Ge)-chelate, bis-(lactamo-*N*-methyl)-*cis*-dichlorogermanes with trimethylsilyltriflate in acetonitrile, proceeds with substitution of one chlorine atom by the triflate group resulting in products with an inversion of configuration at the germanium atom, *viz.* (O → Ge)-chelate bis-(lactamo-*N*-methyl)-*trans*-(trifluorosulfonyloxy)chlorogermanes. This result as well as conductometric studies allow us to suppose an easy ionization of the final products with formation of a triflate anion and a cation with a pentacoordinated germanium atom. According to X-ray structural studies of the prepared compounds, the Ge atom has an octahedral coordination strongly distorted towards a capped trigonal bipyramid configuration. The Ge–Cl bond (2.13–2.17 Å) is the shortest among those observed by us in hypervalent germanium compounds and the Ge–OTf bond is, on the contrary, the longest (3.02–3.36 Å).

1. Introduction

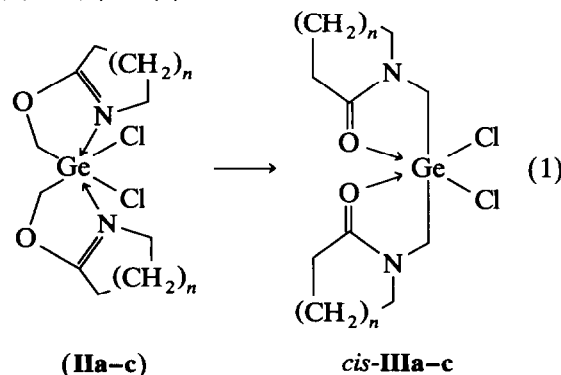
In comparison with pentacoordinated compounds, Si and Ge (*cf. e.g.* reviews [1,2] and refs. therein) compounds with hexacoordinated atoms of these elements have as yet received little attention. However, recently the later compounds have provoked considerable interest as possible intermediates in reactions of compounds with pentacoordinated atoms [3–5]. We have previously shown [4] that on interaction of *N*-trimethylsilyllactames (**Ia–c**) with bis-(chloromethyl)dichlorogermane in a 2:1 ratio under kinetically controlled conditions, the products of *O*-germylmethylation (**IIa–c**) are formed. At elevated temperature, these products are isomerized into thermodynamically more stable products of *N*-germylmethylation, (O → Ge)-chelate bis-(lactamo-*N*-methyl)dichlorogermanes (**IIIa–c**).

According to X-ray structural data, the Ge atom in **IIIa–c** is hexacoordinated and, notably, both chelate

rings (relative to each other) and chlorine atoms have a *cis*-orientation. The Ge–Cl bond lengths in dichlorides **IIIa–c** (2.27–2.31 Å) are somewhat



n = 1 (a), 2 (b), 3 (c)



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* Dedicated to M.G. Voronkov on his 70th birthday.

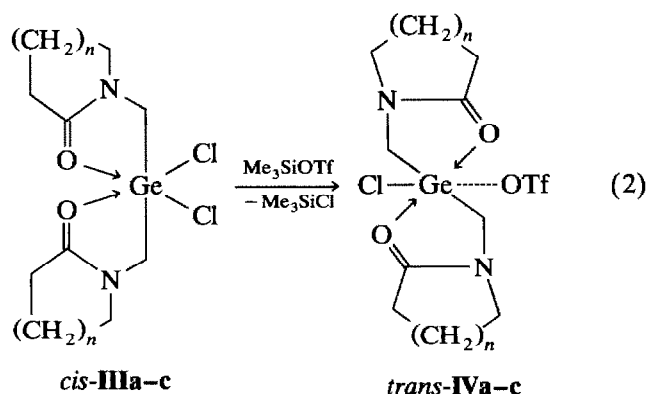
TABLE 1. IR spectra and molar conductivities of compounds **IIIa-c**, **IVa-c**, **Vb** and **VIb**

| Compound | IR spectrum $\nu(\text{N}=\text{C}=\text{O})$ (cm^{-1}) | Conductivity | |
|-------------|--|----------------------------|--|
| | | c (mmol^{-1}) | λ (mSm cm^2 mol^{-1}) |
| IIIa | 1620, 1510 | 6.9 | 39.1 |
| IIIb | 1590, 1510 | 6.7 | 92.5 |
| IIIc | 1580, 1500 | 5.0 | 262 |
| Vb | 1600, 1515 | 1.9 | 85 |
| IVa | 1620, 1510 | 7.4 | 971 |
| IVb | 1600, 1507 | 5.7 | 1154 |
| IVc | 1590, 1510 | 10.0 | 1592 |
| VIb | 1600, 1522 | 7.8 | 358 |

shorter than the corresponding bond lengths in compounds of pentacoordinated germanium (2.32–2.36 Å) [6]. In view of these features, one can expect some decrease in the reactivity of the dichlorides **IIIa-c** in comparison with the chlorides of pentacoordinated Ge in exchange reactions with weak nucleophiles [7]. In the present paper, the reactivity of chlorides **IIIa-c** relative to trimethylsilyltriflate is investigated.

2. Discussion

The reaction proceeds under sufficiently mild conditions (a refluxing of reagent solutions in acetonitrile for a short time) and results in the formation of the substitution products **IVa-c** of one chlorine atom by a triflate group, independent of the ratio of starting reagents. The second chlorine atom substitution is not observed even after treatment of the starting dichlorides **IIIa-c** by excess trimethylsilyltriflate (boiling in acetonitrile for 5 h in a 2:1 ratio).



The structure of the prepared compounds is confirmed by elemental analysis, IR spectra, electroconductivity measurements and an X-ray structural study. As in the starting dichlorides **IIIa-c** [4], the IR spectra of **IVa-c** in the 1700–1500 cm^{-1} region (Table 1)

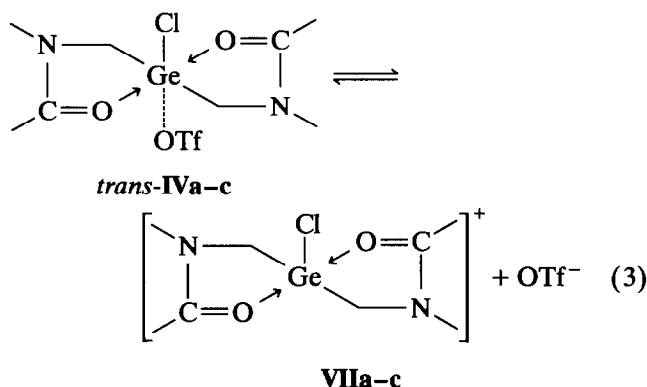
reveal two sufficiently intense absorption bands of strongly coupled $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{N})$ vibrations of amide fragments. These bands are, in fact, identical to those observed for the products of *N*-dimethylchlorogermyl- and *N*-dimethylchlorosilylmethylation of *N*-silyllactames described previously [8,9], testifying to the presence of chelate bidentate lactamomethyl ligands. The absence of the $\nu(\text{C}=\text{O})$ absorption bands due to a non-coordinated carbonyl group proves a hexacoordination of Ge in compounds **IVa-c**.

Electroconductivity measurements of **IIIa-c** and **IVa-c** solutions and, for comparison, of chloride **Vb** and triflate **VIb** of 1-(dimethylgermylmethyl)-2-piperidone in CH_2Cl_2 show that the conductivity of the dichlorides **IIIa-c** and the chloride **Vb**, as well as the previously studied 1-(dimethylchlorosilylmethyl)-2-piperidone [9], is quite low which is characteristic of covalent silylhalogenides. On replacing the chlorine atom by a triflate group, the electroconductivity of triflate increases about fourfold for **VIb** and even by an order of magnitude for **IVa-c** (Table 1). This fact provides a clear indication that the Ge–OTf bond has much more ionic character than the Ge–Cl bond in **IVa-c**. It can also be concluded that in sufficiently polar solvents, molecules of **IVa-c** are to a high degree

TABLE 2. Coordination parameters (Å and °) of the Ge atom in molecules **IVa-c**

| | IVa | IVb | IVc |
|------------------------------------|------------|------------|------------|
| Ge(1)–Cl(1) | 2.159(1) | 2.129(2) | 2.165(1) |
| Ge(1)–O(1) | 2.047(2) | 2.049(5) | 2.012(2) |
| Ge(1)–O(2) | 2.028(2) | 1.984(5) | 1.980(2) |
| Ge(1)–O(3) | 3.015(2) | 3.355(5) | 3.135(2) |
| Ge(1)–C(1) | 1.945(3) | 1.973(7) | 1.941(3) |
| Ge(1)–C(6) | 1.951(4) | 1.923(7) | 1.936(3) |
| Cl(1)–Ge(1)–O(1) | 96.0(1) | 94.7(2) | 92.4(1) |
| Cl(1)–Ge(1)–O(2) | 96.6(1) | 96.5(2) | 93.8(1) |
| Cl(1)–Ge(1)–O(3) | 169.1(1) | 165.3(2) | 165.5(1) |
| Cl(1)–Ge(1)–C(1) | 108.0(1) | 113.5(2) | 109.2(1) |
| Cl(1)–Ge(1)–C(6) | 110.7(1) | 112.9(2) | 107.9(1) |
| O(1)–Ge(1)–O(2) | 167.4(1) | 168.5(2) | 173.8(1) |
| O(1)–Ge(1)–O(3) | 94.2(1) | 70.7(2) | 102.1(1) |
| O(1)–Ge(1)–C(1) | 84.6(1) | 82.1(3) | 83.2(1) |
| O(1)–Ge(1)–C(6) | 90.3(1) | 92.8(3) | 93.5(1) |
| O(2)–Ge(1)–O(3) | 73.3(1) | 98.0(2) | 71.7(1) |
| O(2)–Ge(1)–C(1) | 91.5(1) | 90.8(3) | 94.4(1) |
| O(2)–Ge(1)–C(6) | 85.3(1) | 85.4(3) | 85.0(1) |
| O(3)–Ge(1)–C(1) | 69.0(1) | 63.8(3) | 73.5(1) |
| O(3)–Ge(1)–C(6) | 73.2(1) | 71.0(3) | 71.1(1) |
| C(1)–Ge(1)–C(6) | 141.3(1) | 133.6(3) | 142.9(2) |
| Deviations of Ge(1) from the plane | | | |
| Cl(1)–C(1)–C(6) | 0.015 | 0.018 | 0.024 |
| O(1)–O(2)–C(1)–C(6) | 0.43 | 0.48 | 0.36 |

dissociated with the formation of triflate anions and Ge-containing cations **VIIa-c** with the pentacoordinated Ge atom:



Additional arguments in favour of this conclusion are provided by the X-ray structural study of **IVa-c**, detailed results of which will be published elsewhere. Significant changes in the central atom coordination are observed on substitution of one chlorine atom in **IIIa-c** by a triflate group. On going to **IVa-c**, the octahedral environment of the Ge atom observed in **IIIa-c** [4] shows strong distortion and approaches trigonal bipyramidal (Table 2) as a result of the increase in the Ge-OTf distance to the leaving triflate group (Fig. 1).

In contrast to dichlorides, **IIIa-c** chelate rings in molecules of **IVa-c** formed by the O → Ge coordinative interaction are in *trans*-position to each other. The formation of the O → Ge coordinative bond is favoured by two factors: a high polarity of Ge-OTf and Ge-Cl bonds as well as electron density delocalization in the amide fragment. The Ge(1)-O(3) distance in molecules **IVa-c** varies from 3.02 Å in **IVa** to 3.26 Å in **IVb** which is just about 0.2 Å shorter than the sum of Ge and O van der Waals radii (3.5 Å [10]). At the same time, the

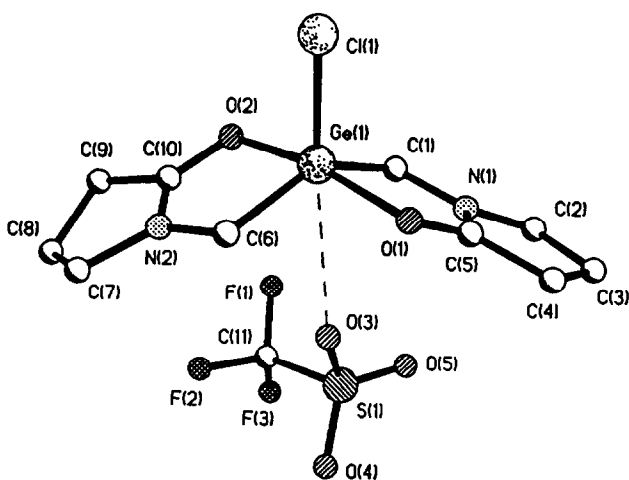


Fig. 1. General view of molecule **IVa**. Hydrogen atoms are omitted.

TABLE 3. X-Ray crystal data for compounds **IVa-c**

| | IVa | IVb | IVc |
|---|-----------------------|---------------------------|------------------------------------|
| <i>a</i> (Å) | 19.339(3) | 16.500(4) | 9.206(2) |
| <i>b</i> (Å) | 11.733(2) | 11.830(4) | 10.212(3) |
| <i>c</i> (Å) | 17.097(2) | 9.607(2) | 21.653(5) |
| β (°) | 117.78(1) | 90 | 92.80(2) |
| <i>V</i> (Å ³) | 3432(2) | 1875(1) | 2033(1) |
| Space group | <i>C</i> 2/ <i>c</i> | <i>Pna</i> 2 ₁ | <i>P</i> 2 ₁ / <i>n</i> |
| <i>Z</i> | 8 | 4 | 4 |
| <i>D</i> _x (g cm ⁻³) | 1.755 | 1.705 | 1.664 |
| <i>N</i> _{ref} (least squares) | 2886 (<i>I</i> > 2σ) | 1725 (<i>I</i> > 2σ) | 3024 (<i>I</i> > 2σ) |
| 2θ _{max} (°) | 56 | 56 | 54 |
| <i>R</i> (<i>R</i> _w) | 0.033(0.031) | 0.045(0.043) | 0.034(0.031) |

Ge-Cl bond lengths in molecules **IVa-c** are 2.13–2.17 Å, i.e. the shortest known among compounds of penta- and hexacoordinated Ge. This structural feature and energetic disadvantage of the further dissociation of cations of **VIIa-c** with formation of germyl dications and chloride anions are, in our view, the main reasons for the substitution of only one chlorine atom by the triflate group in reaction (2).

The stereodynamic behaviour of compounds **IVa-c** and the possibility of the existence of neutral intermediates with one non-chelate ligand and a pentacoordinated Ge atom in equilibrium (3) will be discussed in a separate communication.

3. Experimental details

Crystal data for **IVa-c** are summarized in Table 3. Unit cell parameters and the intensities of the reflections were measured at 190 K with an automated Syntex P2₁ diffractometer (λ(Mo Kα), graphite monochromator, θ–2θ scan). The structures were solved by direct methods and refined by the full-matrix anisotropic least-squares technique. All calculations were carried out using the SHELXTL PLUS programs [11].

IR spectra in thin layers, vaseline oil or MeCN solutions were measured with a Specord IR-75 instrument in KBr cells.

Conductometric measurements were performed with an OK-102/1 conductometer (Radelkis Company, Hungary) with OK-9023 electrodes of three Pt rings in CH₂Cl₂ solution contained in an evacuated electrolytic cell at 25°C. The alternate current frequency was from 80 Hz to 3 kHz. The accuracy of specific conductivity measurements was 13 ± 1%.

Preparation of starting chlorides has been described earlier [4].

(O → Ge)-chelate bis-[(2-oxo-1-pyrrolidinyl)methyl]trifluoro-methanesulfonyloxochlorogermane (**IVa**). A mixture of 0.68 g (0.002 M) of (O → Ge)-chelate bis-[1-(2-oxopyrrolidinyl)methyl]dichlorogermane (**IIIa**) and

0.45 g (0.002 M) of the trimethylsilyl ester of trifluoromethanesulfonic acid in 10 ml of MeCN was refluxed with stirring for 1 h. After solvent evaporation, 0.8 g (88%) of **IVa** was obtained, m.p. 227–230°C. Anal. Found: C 29.25, H 3.69, S 6.95, N 6.79. $C_{11}H_{16}O_5ClF_3$ GeN₂S calc.: C 29.14, H 3.55, S 7.07, N 6.17%. IR (in CHCl₃): $\nu(N-C-O)$ 1620, 1510 cm⁻¹.

(O → Ge)-chelate bis-[(2-oxo-1-piperidinyl)methyl]trifluoromethanesulfonyloxchlorogermane (**IVb**). Under similar conditions, from 0.73 g (0.002 M) of (O → Ge)-chelate bis[1-(2-oxopiperidinyl)methyl]dichlorogermane (**IIIb**) and 0.45 g (0.002 M) of trimethylsilyltriflate, 0.9 g (93%) of **IVb** was obtained, m.p. 191–194°C. IR (in MeCN): $\nu(N-C-O)$ 1600, 1507 cm⁻¹. ¹H NMR: 1.80–1.85 (m, 8H, 2 × 2CH₂); 2.48 (t, 4H, 2CH₂); 3.18 (s, 4H, GeCH₂); 3.49 (t, 4H, 2CH₂N). Anal. Found: C 32.61, H 4.23. $C_{13}H_{20}O_5ClF_3GeN_2S$ calc.: C 32.43, H 4.18%.

Compound **IVb** was also prepared in 76% yield by refluxing 0.73 g (0.002 M) of **IIIb** and 0.9 g (0.004 M) of trimethylsilyltriflate in MeCN for 6 h.

(O → Ge)-chelate bis-[(2-oxo-1-hexahydroazepinyl)methyl]trifluoromethanesulfonyloxchlorogermane (**IVc**). Under similar conditions, from 0.2 g (0.0005 M) of (O → Ge)-chelate bis-[1-(2-oxohexahydroazepinyl)methyl]dichlorogermane (**IIIc**) and 0.12 g (0.0005 M) of trimethylsilyltriflate, 0.23 g (93%) of **IVc** was obtained, m.p. 234–237°C. IR (in CHCl₃): $\nu(N-C-O)$ 1590, 1510 cm⁻¹. Anal. Found: C 35.52, H 5.00, N 5.64. $C_{15}H_{24}O_5ClF_3GeN_2S$ calc.: C 35.42, H 4.74, N 5.49.

Compound **IVc** was also prepared in 71% yield by refluxing 0.2 g (0.0005 M) of **IIIc** and 0.23 g (0.001 M) of trimethylsilyltriflate.

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