Letters to the Editor

Donor-stabilized germylium cations. Bis{[bis((O→Ge)chelato)bis(*N*,*N*-dimethylcarbamoylmethyloxy)]-chloromethylgermylium} hexachlorodimercurate, the first bis-chelate cationic complex of pentacoordinate germanium with 2-hydroxycarboxamides*

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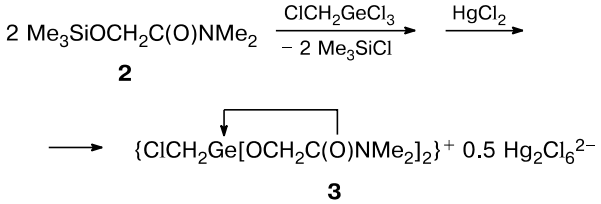
Among cationic complexes of pentacoordinate germanium,[1] which have been extensively studied in recent years, cation-anion complexes containing donor-stabilized germylium cations with (C,O)- and (O,N)-chelate ligands were investigated in sufficient detail (see, for example, Refs 2a—c and references therein). However, data on the structurally characterized (*O*,*O*)-chelate analogs are limited to hexacoordinate acetylacetonate[3a] and 9-oxophenalene[3b] tris-chelates.

Recently, we have described[4] the first representative of neutral pentacoordinate germanium complexes containing (*O*,*O*)-monoanionic bidentate chelate ligands based on 2-hydroxycarboxamides, *viz.*, the (O→Ge)-chelate complex with *O*-[(chloromethyl)dichlorogermyl]mandelic acid *N*,*N*-dimethylamide (**1**). In the present study, we found that the reaction of chloromethyltrichlorogermane with *O*-trimethylsilylglycolic acid *N*,*N*-dimethylamide (**2**) taken in a ratio of 1 : 2 followed by the treatment with $HgCl_2$ affords salt **3**. The latter is a representative of the previously unknown bis-chelate donor-stabilized cationic complexes of pentacoordinate germanium (Scheme 1).

Scheme 1



The intermediate that is formed prior to the treatment with $HgCl_2$ is, apparently, the neutral hexacoordinate bis-chelate complex $ClCH_2Ge(Cl)[OCH_2C(O)NMe_2]_2$.

The X-ray diffraction study showed that the germanium-containing cations are located between the chains

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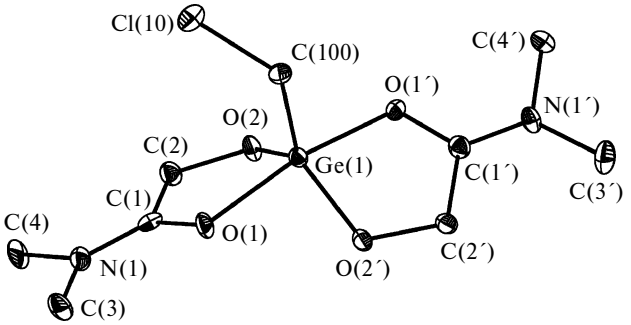

Fig. 1. Structure of cation **3**. The atoms are represented by displacement ellipsoids at the 50% probability level.

Table 1. Selected bond lengths (*d*) and bond angles (ω) in cation **3**

Bond	*d*/Å	Angle	ω/deg
Ge(1)–O(1)	1.960(3)	O(1)–Ge(1)–O(1´)	165.82(14)
Ge(1)–O(1´)	1.963(3)	O(2)–Ge(1)–O(2´)	122.82(15)
Ge(1)–O(2)	1.777(3)	O(1)–Ge(1)–O(2)	85.44(14)
Ge(1)–O(2´)	1.781(3)	O(1)–Ge(1)–O(2´)	88.35(14)
Ge(1)–C(100)	1.936(4)	O(2)–Ge(1)–O(1´)	87.26(14)
O(1)–C(1)	1.281(6)	O(1´)–Ge(1)–O(2´)	85.42(13)
O(2)–C(2)	1.407(5)	C(100)–Ge(1)–O(2)	119.18(18)
		C(100)–Ge(1)–O(2´)	117.99(18)
		C(100)–Ge(1)–O(1)	97.20(17)
		C(100)–Ge(1)–O(1´)	87.26(14)

of the $[HgCl_3^-]_n$ polyanions. The shortest intermolecular distance between the Ge atom and the chlorine atom of the cation (Ge(1)...Cl(10) [$-x + 1, -y, -z + 1$]) is 4.425(1) Å. The distance between the Ge(1) and Cl(1) atoms of the $[HgCl_3^-]_n$ polyanion is 5.390(1) Å. Hence, the interactions of the Ge atom with not only the anion but also with the Cl(10) atom of the chloromethyl group can be reliably excluded.

The cation in the structure of **3** has a bis-chelate structure (Fig. 1, Table 1). The coordination polyhedron of the Ge(1) atom can be described as intermediate between a trigonal bipyramid and a square pyramid. The contribution of the trigonal bipyramid to the coordination polyhedron of the Ge atom[5] is 72%. The equatorial positions are occupied by the O(2), O(2´), and C(100) atoms; the axial positions, by the O(1) and O(1´) atoms. The displacement of the Ge(1) atom from the equatorial plane toward the O(1) atom is 0.007 Å. The O(1)—Ge(1)—O(1´) and O(2)—Ge(1)—O(2´) angles are 165.8(1)° and 122.8(2)°, respectively.

The Ge(1)–O(2) and Ge(1)–O(2´) bond lengths are similar to those in the cationic complex with the *O,N* ligand.[2c] The axial Ge(1)–O(1) and Ge(1)–O(1´) bonds are somewhat shorter than those in the cationic complexes with C,O ligands.[6]

The complete X-ray diffraction data for complex **3** will be published elsewhere.

Bis{[bis((O→Ge)chelato)bis(*N,N*-dimethylcarbamoylmethyloxy)]chloromethylgermylium} hexachlorodimercurate (3). The $ClCH_2GeCl_3$ compound (1.14 g, 0.005 mol) was added dropwise with stirring to a solution of compound **2** (1.75 g, 0.01 mol) in $CHCl_3$ (5 mL). The reaction mixture was allowed to stand for 16 h and then refluxed for 1 h. The solvent was removed by evaporation, the oily residue was dissolved in CH_3CN (5 mL), and $HgCl_2$ (1.54 g) was added to the solution. The crystals that precipitated after 1 day were filtered off. The yield of complex **3** was 2.2 g (70%), m.p. 221—222 °C (CH_3CN). Found (%): C, 17.04; H, 2.86; N, 4.31. $C_{18}H_{36}Cl_8Ge_2Hg_2N_4O_8$. Calculated (%): C, 17.07; H, 2.86; N, 4.42. IR (Specord IR-75, KBr cell, CH_3CN), ν/cm^{-1}: 1660 (NCO). ^{1}H NMR (Varian XL-400, 400.1 MHz, CD_3CN), δ: 2.99 and 3.15 (both s, 3 H each, NMe_2); 3.49 and 3.53 (both d, 1 H each, CH_2Cl, $^2J_{H,H}$ = 11.4 Hz); 4.59 and 4.64 (both d, 2 H each, CH_2O, $^2J_{H,H}$ = 4.5 Hz).

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