Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Chloridobis[(2-oxoazocan-1-yl)methyl]germanium(IV) trifluoromethanesulfonate

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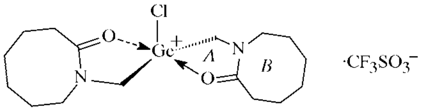
Received 18 December 2006
Accepted 21 February 2007
Online 17 March 2007

In the title compound, $[Ge(C_8H_{14}NO)_2Cl]CF_3SO_3$, which is the first complex containing an eight-membered lactam (enantholactam) as ligand, the coordination polyhedron of the Ge^{IV} atom is intermediate between trigonal–bipyramidal and square-pyramidal. Quantum chemical calculations of the crystal structure indicate the absence of additional coordination bonding between the Ge^{IV} atom and the trifluoromethanesulfonate anion.

Comment

Pentacoordinate silylium cations stabilized by intramolecular (intraionic) N→Si and O→Si coordination interactions have been extensively and systematically studied, in contrast with their germanium analogues (see reviews: Kost & Kalikhman, 2004; Baukov & Tandura, 2002, and references therein). Previously (Baukov *et al.*, 1993), we have found that the reactions of bis(lactamomethyl)dichlorogermanes $(L^nCH_2)_2$-$GeCl_2$ (where *L* is a bidentate lactamomethyl *C*,*O*-chelating ligand and *n* is the size of the lactam ring, 5–7) with Me_3SiOTf (Tf is trifluoromethanesulfonate) afforded monochlorides $(L^nCH_2)_2Ge(Cl)OTf$ in which the C and O atoms and the monodentate ligands are arranged *trans* with respect to each other. Compared with covalent dichlorides, the latter compounds show higher conductivity in CH_2Cl_2, which suggests the presence of the germylium ion $[(L^nCH_2)_2$-$Ge(Cl)]^+$ stabilized by two intra-ionic O→Ge coordination bonds in solution. As a continuation and development of our work in this area (Baukov *et al.*, 1994, 1993; Bylikin *et al.*, 1997, 2003; Ovchinnikov, Struchkov, Baukov, Shipov & Bylikin, 1994; Ovchinnikov, Struchkov, Baukov, Shipov, Kramarova & Bylikin, 1994; Kramarova *et al.*, 2004; Korlyukov *et al.*, 2006), the title compound, (I), has been studied. This compound is the first representative of complexes containing an eight-membered lactam as ligand, the chloride–trifluoromethanesulfonate $(L^8CH_2)_2Ge(Cl)OTf$ (Fig. 1).



(I)

The most important parameters of (I) are listed in Table 1. The germyl cation has a bis-chelate structure. Atom Ge1 participates in two five-membered rings. These rings form a fused cyclic system with the eight-membered ring, sharing atoms N1 and C7. The deviation of atom Ge1 from the plane of the equatorial atoms C1, C1′ and Cl1 towards atom O1 is 0.014 (1) Å, while the O1—Ge1—O1′ and C1—Ge1—C1′ angles are 173.02 (4) and 144.86 (7)°, respectively. According to Tamao *et al.* (1992), these values indicate that the coordination polyhedron cannot be described as ordinary trigonal–bipyramidal (TBP). The estimation of the contribution of TBP by the formula %TBP = 100(O1—Ge1—O1′ − C1—Ge1—C1′)/60 gives a magnitude of approximately 47% [taken from Kost *et al.* (2002)]. Thus, the coordination polyhedron of atom Ge1 is intermediate between trigonal–bipyramidal and square-pyramidal.

Previously, we reported structural data for a number of compounds with nearly identical coordination of Ge (Baukov *et al.*, 1994, 1993; Bylikin *et al.*, 1997; Ovchinnikov, Struchkov, Baukov, Shipov & Bylikin, 1994; Ovchinnikov, Struchkov, Baukov, Shipov, Kramarova & Bylikin, 1994). The Ge—O bonds and O—Ge—O angles in those compounds vary in the ranges 1.98–2.05 Å and 167–176°, respectively. Thus, the Ge1—O1 and Ge1—O1′ bonds and the equatorial Ge—C and Ge—Cl bonds in (I) (Table 1) are within the ranges for similar compounds, (II)–(VI) (defined in Fig. 2). Comparison of the structural parameters of (I) (Table 1) with those of compounds (II)–(VI) shows that the coordination polyhedron of the Ge atom is very stable and its geometry is only slightly affected by the nature of the fused bicyclic coordination environment. For brevity, we denote five- and eight-membered rings as *A* (*A*′) and *B* (*B*′), respectively. Both *A* and *A*′ rings have an envelope conformation, with atom Ge1 deviating by 0.301 (2) and 0.273 (2) Å, respectively. Details of the ring puckering of rings *B* and *B*′ are presented in Table 2 (Cremer & Pople, 1975). Rings *B* are bent along the C8···C3 vector. The conformation of the latter rings may be described as 'boat–chair', with atoms C5 and C6 deviating on opposite sides of the plane of atoms C3/C4/C7/C8.

In contrast with the influence of the nature of ring *B*, the effect of crystal packing on the geometry of the Ge coordination centre is somewhat more pronounced. The Ge—Cl bond lengths are in the range 2.13–2.22 Å. The particular reason for such variation is the presence of short Ge···*X* contacts with the counter-ion. The interatomic Ge···*X* distances are less than or equal to the sum of the van der Waals radii of Ge, O and I (the sum of the Ge and O radii is 3.5 Å, while that of Ge and I is 4.2 Å; Gar *et al.*, 1987). The longest Ge—Cl bonds and the shortest Ge···O distances correspond to I^- and I^{3-} counter-ions (Ovchinnikov, Struchkov, Baukov, Shipov, Kramarova & Bylikin, 1994; Bylikin *et al.*, 1997). In general, the Ge—Cl bond lengths are defined by the dimensions of the counter-ion and ring *B*. In the case of the five-membered ring *B* in (II), the Ge···O distance is shorter than in the case of six- and seven-membered rings *B* by 0.1–0.2 Å. In turn, in the case of (III) (six-membered ring *B*), in which the longest Ge···O distance is observed, the Ge—Cl bond length is decreased by 0.03 Å compared with (II). In (I), the Ge1—Cl1 bond length is almost equal to that in (II). However, the Ge1···O1*T* interatomic distance is longer than that in (II) by 0.3 Å. The most reliable explanation of the observed distances is the presence of an additional Ge1···O2*T* contact, with an interatomic distance of 3.433 (2) Å. A similar tendency is observed for structure (V). The Ge···I distance in three independent molecules varies in the range 4.18–4.22 Å, which causes changes in the Ge—Cl bonds which are in the range 2.17–2.21 Å.

Analysis of these geometric parameters does not allow us to estimate the role of the cation–anion interaction. According to quantum chemical calculations of the [PhGe(OCH$_2$CH$_2$NMe$_2$)$_2$]Cl cation–anion pair (Khrustalev *et al.*, 2006), we can suggest that the crystal structure of (I) is a model for cation–anion pairs that might exist in solution. The nature of the cation–anion interaction in (I) is still an open question. Taking into account the elongation of the Ge—Cl bond, we previously considered the Ge···*X* interaction as a weak coordination bond. Thus, the coordination of Ge1 was usually considered as 5+1 (distorted octahedron). To clarify the nature of such an interaction, we carried out quantum chemistry calculations of the crystal structure of (I) using the *VASP* program (Kresse, 1993; Kresse & Furthmuller, 1996*a*,*b*; Kresse & Hafner, 1993) and density functional theory (DFT; PBE exchange-correlation functional). Optimized structural parameters are close to the experimental parameters. The calculation leads to increases in the Ge1···O1*T* and Ge1···O2*T* interatomic distances of 0.05 and 0.1 Å, respectively. Such errors in the definitions of weak interatomic contacts are typical for DFT functions, which cannot account for non-local dispersion interactions. The geometry of the Ge1 coordination centre is reproduced with higher accuracy, the mean deviation in the bond lengths being 0.02 Å.

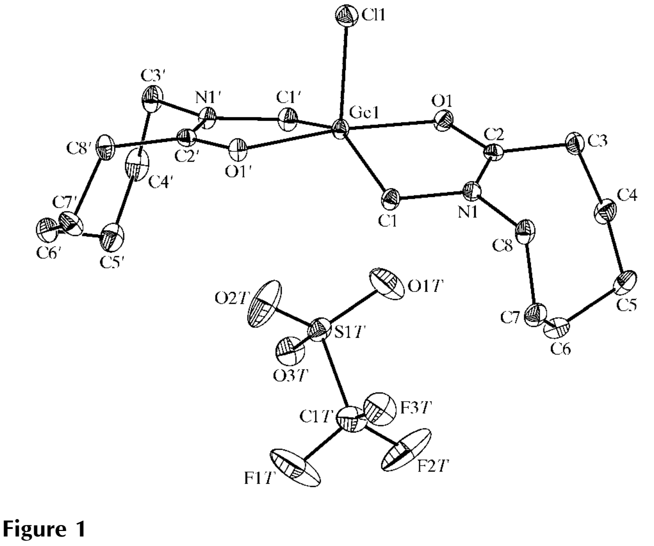


Figure 1
The structure of the cation–anion pair of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

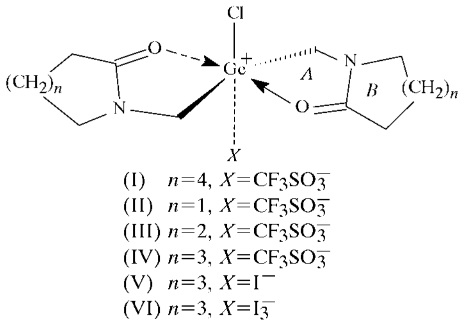


Figure 2
General view and legend for the structures of compounds (II)–(VI).

The chemical bonding pattern in the structure of (I) was analyzed in terms of Bader's 'atoms in molecules' theory (AIM) using the calculated electron-density function. For calculation of the energy of the interatomic contacts, we utilized the correlation formula of Espinosa *et al.* (1998). This formula establishes a relation between the energy of an interatomic contact and the value of the potential energy density at a critical point CP(3, −1). The location of CP(3, −1) between two atoms according to AIM theory corresponds to the presence of an interatomic interaction. Analysis of the electron-density function in terms of AIM theory has shown the absence of CP(3, −1) between atoms Ge1 and O of the trifluoromethanesulfonate group. Thus, a coordination bond between atom Ge1 and atom O1*T* or O2*T* in (I) does not exist and the Ge···O interaction can be considered as a dispersion one. Besides, atoms O1*T* and O2*T* participate in weak (0.9–1.9 kcal mol^{-1}; 1 kcal mol^{-1} = 4.184 kJ mol^{-1}) C—H···O interactions with atoms H6*A*, H8*A*, H1*B*, H1′*B* and H5′*A* of the eight-membered rings (calculated distances 2.41–2.71 Å). In the similar compounds (II)–(VI), the Ge···O(*X*) interactions are unlikely to be much stronger than those in (I). Thus, one can conclude that the coordination of atom Ge1 in compounds (I)–(VI) should be described as 5 rather than 5+1. Possibly the Ge···O distance, which is longer than 3 Å, appears to be insufficient for the formation of a coordinative bond between the cation and anion.

Experimental

For the preparation of the (O→Ge)-bischelate chloridobis[(2-oxoazocan-1-yl)methyl]germanium(IV) trifluoromethanesulfonate, (I), a mixture of (O→Ge)-bischelate dichloridobis[(2-oxoazocan-1-yl)-methyl]germanium(IV), the preparation of which will be reported elsewhere (1.06 g, 25 mmol), and Me$_3$SiOTf (0.6 g, 25 mmol) in MeCN (25 ml) was refluxed for 2 h. The volatiles were removed *in*

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vacuo, and the crystalline residue was washed with diethyl ether and dried *in vacuo* to yield 1.32 g (98%) of (I) (m.p. 528–531 K) (recrystallized from benzene–acetonitrile, 10:1 *v*/*v*). IR (Specord IR-75 spectrometer; KBr cell, $CHCl_3$, ν, cm^{-1}): 1580, 1490 (NCO); ^1H NMR (Varian XL-400 spectrometer; 400.1 MHz, $CDCl_3$): δ 1.13–2.00 (*m*, 16H, H4–H7), 2.64 (*br m*, 4H, H3), 3.11 (*br m*, 4H, NCH_2), 3.70 (*br m*, 4H, H8). Analysis found: C 37.84, H 5.32, N 5.27%; calculated for $C_{17}H_{28}ClF_3GeN_2O_5S$: C 37.98, H 5.25, N 5.21%.

Crystal data

$[Ge(C_8H_{14}NO)_2Cl]CF_3O_3S$
M_r = 537.54
Monoclinic, $P2_1/c$
a = 14.3288 (5) Å
b = 12.0353 (4) Å
c = 13.1364 (5) Å
β = 108.1310 (10)°
V = 2152.91 (13) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 1.70 mm^{-1}
T = 100 (2) K
0.05 × 0.05 × 0.04 mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
T_{min} = 0.849, T_{max} = 0.942
51328 measured reflections
7284 independent reflections
5148 reflections with $I > 2\sigma(I)$
R_{int} = 0.073

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.065
S = 1.00
7284 reflections
271 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.50 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.49 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °) for (I).

Ge1—Cl1	2.1678 (4)	O1—Ge1—O1′	173.02 (4)
Ge1—C1	1.941 (1)	C1—Ge1—C1′	144.86 (7)
Ge1—C1′	1.945 (1)	Ge1···O1*T*	3.310 (2)
Ge1—O1	2.004 (1)	Ge1···O2*T*	3.433 (2)
Ge1—O1′	1.982 (1)	Ge1···Δ_1	0.014 (1)
C2—O1	1.277 (2)	MD Δ_2	0.0111
C2′—O1′	1.279 (2)	MD Δ_3	0.0212
C2—N1	1.326 (2)	Ge1–Δ_2	0.301 (2)
C2′—N1′	1.329 (2)	Ge1–Δ_3	0.273 (2)

Notes: MD denotes the mean deviation from the plane Δ_n (Å); Δ_1 is the plane of atoms C1/C1′/Cl1, Δ_2 is the plane of atoms C1/N1/C2/O1 and Δ_3 is the plane of atoms C1′/N1′/C2′/O1′.

Table 2
Parameters (Å, °) illustrating the ring puckering of rings *B* and *B*′.

B and *B*′ correspond to rings N1/C2–C8 and N1′/C2′–C8′, respectively.

Parameter	*B*	*B*′
Q_2	0.8677 (18)	0.8457 (18)
Q_3	0.6965 (17)	0.7064 (17)
Q_4	−0.3042 (17)	−0.2890 (17)
φ_2	289.16 (11)	290.94 (12)
φ_3	327.58 (14)	328.10 (14)
MD Δ_4	0.0054	0.0145
MD Δ_5	0.0405	0.0359
Δ_4–Δ_5 angle	68.91 (8)	69.11 (8)

Notes: MD denotes the mean deviation from the plane Δ_n (Å); Δ_4 is the plane of atoms C8/C2/N1/C3 and Δ_5 is the plane of atoms C7/C8/C3/C4.

H atoms were positioned geometrically and refined in a rigid-body model, with C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the Russian Foundation for Basic Research (grant No. 05-03-32964) and the International Association for the Promotion of Cooperation with Scientists from the Independent States of the Former Soviet Union (INTAS, Project No. 03-51-4164).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3085). Services for accessing these data are described at the back of the journal.

References

Baukov, Yu. I., Shipov, A. G., Ovchinnikov, Yu. E. & Struchkov, Yu. T. (1994). *Russ. Chem. Bull.* **43**, 917–928.

Baukov, Yu. I., Shipov, A. G., Smirnova, L. S., Kramarova, E. P., Bylikin, S. Yu., Ovchinnikov, Yu. E. & Struchkov, Yu. T. (1993). *J. Organomet. Chem.* **461**, 39–42.

Baukov, Yu. I. & Tandura, S. N. (2002). *The Chemistry of Organic Germanium, Tin and Lead Compounds*, edited by Z. Rappoport, pp. 961–1239. Chichester: Wiley.

Bruker (2005). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bylikin, S. Yu., Kramarova, E. P., Pogozhikh, S. A., Shipov, A. G., Negrebetsky, V. V., Ovchinnikov, Yu. E. & Baukov, Yu. I. (2003). *Russ. Chem. Bull.* **52**, 1720–1729.

Bylikin, S. Yu., Shipov, A. G., Kramarova, E. P., Negrebetsky, V. V., Smirnova, L. S., Pogozhikh, S. A., Ovchinnikov, Yu. E. & Baukov, Yu. I. (1997). *Zh. Obshch. Khim.* **67**, 1850–1865. (In Russian.)

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Espinosa, E., Molins, E. & Lecomte, C. (1998). *Chem. Phys. Lett.* **285**, 170–173.

Gar, T. K., Viktorov, N. A., Gurkova, S. N., Gusev, A. I. & Alekseev, N. V. (1987). *J. Struct. Chem. (Engl. Transl.)*, **28**, 161–162.

Khrustalev, V. N., Portnyagin, I. A., Borisova, I. V., Zemlyansky, N. N., Ustynyuk, Y. A., Antipin, M. Yu. & Nechaev, M. S. (2006). *Organometallics*, **25**, 2501–2504.

Korlyukov, A. A., Pogozhikh, S. A., Ovchinnikov, Yu. E., Lyssenko, K. A., Antipin, M. Yu., Shipov, A. G., Zamyshlyaeva, O. A., Kramarova, E. P., Negrebetsky, V. V., Yakovlev, I. P. & Baukov, Yu. I. (2006). *J. Organomet. Chem.* **691**, 3962–3975.

Kost, D. & Kalikhman, I. (2004). *Adv. Organomet. Chem.* **50**, 1–106.

Kost, D., Kingston, V., Gostevski, B., Ellern, A., Stalke, D., Walfort, B. & Kalikhman, I. (2002). *Organometallics*, **21**, 2293–2305.

Kramarova, E. P., Korlyukov, A. A., Bylikin, S. Yu., Shipov, A. G., Baukov, Yu. I. & Kost, D. (2004). *Russ. Chem. Bull.* **53**, 1135–1136.

Kresse, G. (1993). Thesis, Technical University of Vienna, Austria.

Kresse, G. & Furthmuller, J. (1996*a*). *Comput. Mater. Sci.* **6**, 15–50.

Kresse, G. & Furthmuller, J. (1996*b*). *Phys. Rev. B*, **54**, 11169–11186.

Kresse, G. & Hafner, J. (1993). *Phys. Rev. B*, **47**, 558–561.

Ovchinnikov, Yu. E., Struchkov, Yu. T., Baukov, Yu. I., Shipov, A. G. & Bylikin, S. Yu. (1994). *Russ. Chem. Bull.* **43**, 1351–1355.

Ovchinnikov, Yu. E., Struchkov, Yu. T., Baukov, Yu. I., Shipov, A. G., Kramarova, E. P. & Bylikin, S. Yu. (1994). *Russ. Chem. Bull.* **43**, 1346–1350.

Sheldrick, G. M. (1998). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Tamao, K., Hayashi, T., Ito, Y. & Shiro, M. (1992). *Organometallics*, **11**, 2099–2114.

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