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***trans*-Tetrabromobis(3,5-dimethylpyridine)-germanium(IV), a non-merohedral twin**

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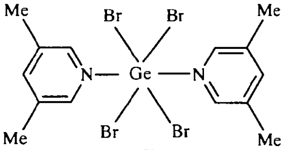
Abstract

The structure of the title compound, $[GeBr_4(C_7H_9N)_2]$, is the first example of an addition compound of $GeBr_4$ with two aromatic nitrogen bases. The molecule, with D_{2h} symmetry, has crystallographic C_{2h} site symmetry. The environment around the Ge atom can be described as a slightly distorted octahedron with the dimethylpyridine ligands occupying axial positions and the four bromo ligands in the equatorial plane. The crystal structure is a non-merohedral twin composed of two overlapping monoclinic domains, simulating an orthorhombic symmetry.

Comment

The tetrahalides of germanium, as an element of the fourth period, form interesting Lewis acid–base complexes. Addition of a Lewis base increases the coordination number of the germanium centre from four to five (Bilton & Webster, 1972) or six (Abel, 1958; Fergusson *et al.*, 1959; Hulme *et al.*, 1960; Muetterties, 1960). A similar reaction is shown by the tetrahalides of silicon (Wannagat *et al.*, 1954, 1968; Beattie *et al.*, 1964; Mayr-Stein, 1998; Spangenberg, 1999). We present here the first structure of an addition compound of $GeBr_4$ with aromatic nitrogen bases as part of our studies on the structure and properties of germanium tetrahalides and tertiary amines. The title compound, (I), belongs to the symmetry point group C_{2h} (deviating only slightly from molecular D_{2h} symmetry), with the Ge atom on a special position of site symmetry 2/*m* and the dimethylpyridine moieties located on a crystallographic mirror plane. Only the Br atoms and two H atoms of each methyl group occupy a general position. The Ge centre appears in a nearly ideal octahedral environment, where the two dimethylpyridine ligands occupy axial positions and the four bromo ligands lie in the equatorial plane. There are only minor deviations from the perfect octahedral coordination.



(I)

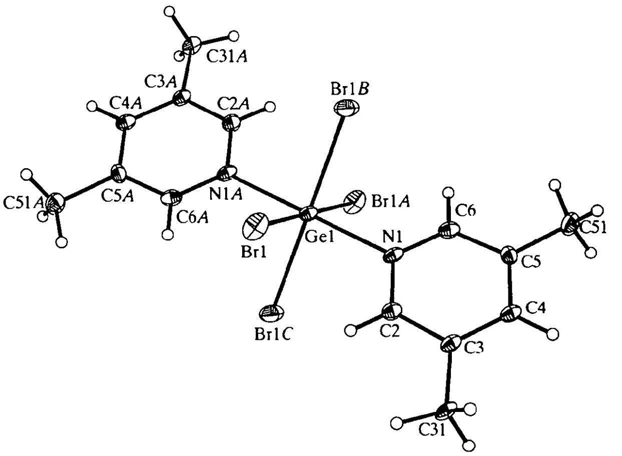


Fig. 1. Perspective view of (I) with the atom-numbering scheme and displacement ellipsoids at the 50% probability level.

Experimental

Germanium tetrabromide was dissolved in *n*-pentane under an atmosphere of dry nitrogen. After adding 3,5-dimethylpyridine at room temperature with stirring, the solid product was filtered under a dry nitrogen atmosphere, dried *in vacuo* and dissolved in hot chloroform. Single crystals of the title compound were obtained after slow cooling. Analysis measured (calculated): C 28.4 (27.7), H 3.23 (2.97), N 4.69 (4.62), Br 51.8% (52.7%).

Crystal data

$[GeBr_4(C_7H_9N)_2]$
$M_r = 606.53$
Monoclinic
$C2/m$
$a = 16.318\,(1)$ Å
$b = 7.362\,(1)$ Å
$c = 8.229\,(1)$ Å
$\beta = 113.09\,(1)°$
$V = 909.38\,(17)$ Å^3
$Z = 2$
$D_x = 2.215$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4554 reflections
$\theta = 1–25°$
$\mu = 10.467$ mm^{-1}
$T = 173\,(2)$ K
Cube
0.20 × 0.20 × 0.20 mm
Light yellow

Data collection

Siemens CCD three-circle diffractometer
6623 reflections with $I > 2\sigma(I)$

ω scans
Absorption correction:
empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.108$, $T_{\max} = 0.123$
9321 measured reflections
9321 independent reflections

$\theta_{\max} = 27.10°$
$h = -20 \rightarrow 20$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$
104 standard reflections
frequency: 1200 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.159$
$S = 0.998$
9321 reflections
63 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0750P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.871$ e Å^{-3}
$\Delta\rho_{\min} = -0.973$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ge1—N1	2.112 (3)	Ge1—Br1	2.4458 (4)
N1—Ge1—Br1	90.48 (8)	C6—N1—Ge1	121.6 (3)
C6—N1—C2	119.0 (3)	C2—N1—Ge1	119.4 (3)
Br1—Ge1—N1—C2	45.543 (10)		

Three sets of 50 frames each at different values of φ and θ were used to extract 128 reflections for determination of a preliminary cell. The indexing procedure yielded an orthorhombic C-centred cell ($a = 7.34$, $b = 16.28$, $c = 37.71$ Å and $V = 4507$ Å^3) using all reflections. Thus, the collected frames were integrated using this orthorhombic cell, but after data reduction, no acceptable space group could be identified and structure solution was impossible. The reflection data showed several classes of weak reflections, but no sensible extinction conditions. However, a thorough inspection of the reciprocal space revealed that, instead of the orthorhombic cell, two monoclinic C-centred cells (related by a mirror plane perpendicular to the orthorhombic c^* axis) could be fitted to the reflection data. The reflections of the two twin components were separated sufficiently, but overlap occurred for reflections with $h = 5m$ (with m integer). After transforming the data from the orthorhombic to the monoclinic cell, using the transformation matrix $(0\bar{1}0/\bar{1}00/0,\frac{1}{5},-\frac{1}{5})$ for the direct cell parameters and the reflection indices, the resulting space group was now $C2/m$ and the structure could be solved.

For refinement with *SHELXL*97 (Sheldrick, 1997), the twin law $(1,0,-\frac{2}{5}/010/00\bar{1})$ had to be applied to the reflection data. This means that the file containing the reflection data had to be modified by adding for every reflection with $h = 5m$ its twin counterpart (with the indices $h_{\rm twin} = h$, $k_{\rm twin} = k$, $l_{\rm twin} = -0.4h - l$). The modified reflection data were read in *via HKLF*5 and an additional variable was introduced (using the *BASF* command) describing the fractional contributions of the two twin components; the ratio finally refined to 0.449 (2):0.551 (2).

All H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters [$U(\rm H) = 1.2U_{eq}(C)$ or $U(\rm H) = 1.5U_{eq}(C_{methyl})$] using a riding model with aromatic C—H = 0.95 Å or methyl C—H = 0.98 Å.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1320). Services for accessing these data are described at the back of the journal.

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Phase transition in bis(ethyldimethylammonium) pentachloroantimonate(III)

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Abstract

The crystal structure of a new member of the alkylammonium chloroantimonate family, namely bis(ethyldimethylammonium) pentachloroantimonate(III), $[C_2H_5NH(CH_3)_2]_2[SbCl_5]$, was determined at room temperature. The anionic sublattice consists of isolated distorted square-pyramidal $[SbCl_5]^{2-}$ units and

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