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Bis(*tert*-butylthiolato-*S*)germanium–Imide Trimer

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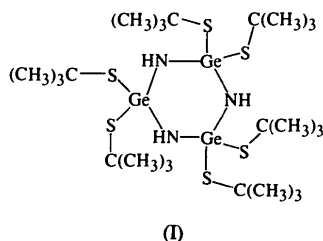
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Abstract

The cyclic germanium (IV) imide thiolate, *cyclo*-tri- μ -imido-tris[bis(*tert*-butylthiolato-*S*)germanium], $[\text{Ge}_3\{(\text{CH}_3)_3\text{CS}\}_6(\text{NH})_3]$, was synthesized and its absolute structure determined. The six-membered ring formed by the trimer has a greater non-planarity than the only other reported Ge^{IV} -imide trimer. The Ge—N ring distances range from 1.755 (13) to 1.829 (12) Å and average 1.807 Å. The Ge—S distances range from 2.171 (4) to 2.272 (5) Å and average 2.218 Å.

Comment

The structure determination of the title compound, (I), was undertaken in order to positively identify the compound and determine the degree of oligomerization.



The Ge_3N_3 ring is puckered, with the N atoms deviating from the plane formed by the three Ge atoms by 0.11 (2), 0.14 (2) and -0.50 (1) Å for atoms N1, N2 and N3, respectively (Fig. 1). This non-planarity is greater than is seen in $(\text{Cl}_2\text{GeNCH}_3)_3$, which has N-atom deviations in the range -0.01 to 0.23 Å (Ziegler & Weiss, 1971). Steric effects of the bulky *tert*-butylthiolate groups may account for the greater puckering. The puckered ring forms a fold along the line connecting the Ge2 and N3 atoms producing two four-membered least-squares planes [maximum deviation from the mean plane of 0.03 (2) Å], with a dihedral angle between the planes of 25.3 (5)°. The N—Ge—N angles are slightly smaller and the Ge—N—Ge angles slightly larger than in $(\text{Cl}_2\text{GeNCH}_3)_3$, which has comparable Ge—N distances of 1.78 (2)–1.86 (2) Å.

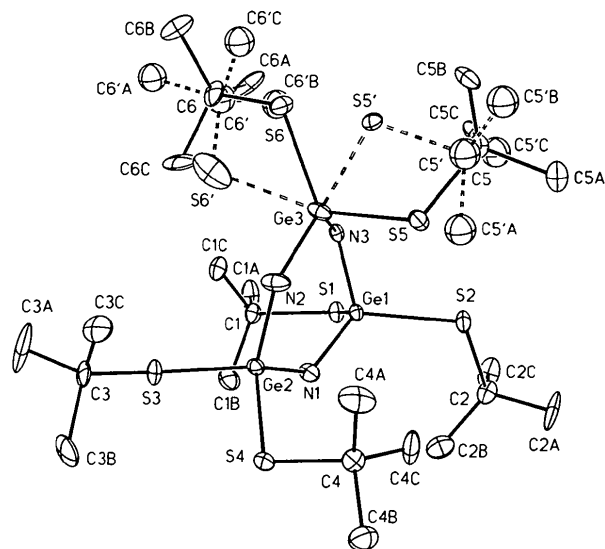


Fig. 1. Displacement-ellipsoid plot of the title compound drawn at the 20% probability level. H atoms have been omitted for clarity. The lower occupancy disordered *tert*-butylthiolate groups are shown with dashed bonds.

The Ge^{II} -imide trimer $[\text{GeN}\{(\text{CH}_3)_2\text{CH}\}\text{C}_6\text{H}_3]_3$ (Bartlett & Power, 1990) forms a planar ring and has distances and angles similar to those of the title compound. All Ge—S distances here are similar to the distances of 2.261 (3) and 2.255 (4) Å (Veith, Detemple & Huch, 1990), and of 2.199 (2) and 2.195 (2) Å (Pfeiffer, Noltemeyer & Meller, 1989) found in other Ge^{IV} thiolates. The S—Ge—S angles are comparable to those in $[\text{Ge}(\text{SC}_6\text{H}_4\text{CH}_3)]_4$ (Kersting & Krebs, 1994). The complex is chiral due to the S—C arms which form a handed screw. Both thiolate groups attached to the Ge3 atom are disordered. The *tert*-butylthiolate groups are displaced by *ca.* 53° from the higher occupancy positions, but the central C atoms of the respective *tert*-butyl groups remain essentially fixed.

Experimental

In a reaction aimed at synthesizing $(\text{Me}_3\text{CS})_3\text{GeNH}_2$ (Mehra, Gupta & Sukhani, 1967), GeCl_4 (2.97 g, 14.0 mmol) and Me_3CSH (3.92 g, 43.5 mmol) were condensed into 50 ml of anhydrous benzene in a 100 ml H-tube under vacuum. The mixture was warmed slowly to dissolve the contents and then 90 mmol of anhydrous NH_3 was condensed in at 77 K. This mixture was warmed slowly to room temperature and stirred for one day. Following filtration and evaporation to dryness, the waxy solid obtained was recrystallized twice under an inert atmosphere from hot dry heptane to afford 0.269 g of $[\text{Ge}(\text{NH})(\text{SCMe}_3)_2]_3$ as a minor product. ^1H NMR (C_6D_6): δ 1.598 (CH₃), 1.51 (NH); ^{13}C NMR: δ 35.5 (CH₃), 48.1 (C); IR (cm^{-1}): 3397, 3383 [N—H (*s*)]. The data crystal was mounted in a sealed glass capillary under an inert atmosphere and the data were collected at 223 K. The low-temperature apparatus restricts the data collection to θ of less than 60°.

Crystal data

[Ge₃(C₄H₉S)₆(NH)₃] $M_r = 797.86$

Monoclinic

 $P2_1$ $a = 12.013 (2) \text{ \AA}$ $b = 10.610 (2) \text{ \AA}$ $c = 15.634 (3) \text{ \AA}$ $\beta = 103.08 (3)^\circ$ $V = 1940.9 (7) \text{ \AA}^3$ $Z = 2$ $D_x = 1.365 \text{ Mg m}^{-3}$ D_m not measuredCu $K\alpha$ radiation $\lambda = 1.54178 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 5.25\text{--}27.40^\circ$ $\mu = 5.884 \text{ mm}^{-1}$ $T = 243 (2) \text{ K}$

Irregular

 $0.48 \times 0.42 \times 0.31 \text{ mm}$

Translucent

C2C	0.025 (2)	0.609 (2)	0.458 (1)	0.065 (6)
C3	0.295 (2)	0.397 (2)	-0.069 (1)	0.053 (6)
C3A	0.324 (3)	0.260 (3)	-0.084 (2)	0.129 (15)
C3B	0.203 (2)	0.437 (3)	-0.147 (1)	0.080 (9)
C3C	0.397 (2)	0.484 (3)	-0.059 (1)	0.080 (9)
C4	0.181 (1)	0.872 (2)	0.041 (1)	0.039 (4)
C4A	0.301 (2)	0.917 (2)	0.051 (2)	0.069 (7)
C4B	0.099 (2)	0.951 (2)	-0.023 (1)	0.059 (6)
C4C	0.146 (2)	0.874 (2)	0.130 (1)	0.068 (7)
S5†	0.4816 (5)	0.8191 (5)	0.2828 (4)	0.0367 (16)
C5†	0.569 (2)	0.850 (2)	0.394 (1)	0.035 (6)
C5A†	0.520 (2)	0.978 (3)	0.422 (2)	0.056 (7)
C5B†	0.694 (2)	0.869 (3)	0.393 (2)	0.050 (8)
C5C†	0.553 (2)	0.750 (3)	0.459 (1)	0.043 (7)
S5'‡	0.6292 (9)	0.7140 (14)	0.3211 (9)	0.031 (5)
C5'‡	0.561 (6)	0.836 (6)	0.377 (5)	0.080
C5' C‡	0.522 (10)	0.795 (12)	0.458 (6)	0.080
C5' B‡	0.657 (7)	0.930 (11)	0.398 (7)	0.080
C5' A‡	0.463 (7)	0.880 (12)	0.306 (6)	0.080
S6†	0.6548 (4)	0.5503 (5)	0.2823 (4)	0.041 (2)
C6†	0.659 (1)	0.375 (1)	0.278 (1)	0.051 (7)
C6A†	0.636 (2)	0.326 (2)	0.364 (2)	0.066 (10)
C6B†	0.780 (2)	0.341 (2)	0.274 (2)	0.073 (10)
C6C†	0.558 (1)	0.351 (1)	0.202 (1)	0.13 (3)
S6'‡	0.554 (1)	0.442 (1)	0.201 (1)	0.103 (15)
C6'‡	0.649 (1)	0.384 (1)	0.281 (1)	0.080
C6' C‡	0.757 (1)	0.467 (1)	0.297 (1)	0.080
C6' B‡	0.603 (1)	0.386 (1)	0.365 (1)	0.080
C6' A‡	0.682 (1)	0.239 (1)	0.260 (1)	0.080

† Site occupancy of 0.746 (10). ‡ Site occupancy of 0.254 (10).

Data collection

Siemens P4 diffractometer

 $\theta/2\theta$ scans

Absorption correction:

semi-empirical via

 ψ scans (XPREP in

SHELXTL; Sheldrick,

1994)

 $T_{\min} = 0.036$, $T_{\max} = 0.162$

3160 measured reflections

2904 independent reflections

2643 observed reflections

 $[I > 2\sigma(I)]$ $R_{\text{int}} = 0.0211$ $\theta_{\text{max}} = 58.21^\circ$ $h = 0 \rightarrow 13$ $k = -11 \rightarrow 2$ $l = -17 \rightarrow 16$

3 standard reflections

monitored every 97

reflections

intensity decay: 3.1%

Refinement

Refinement on F^2 $R(F) = 0.0512$ $wR(F^2) = 0.1320$ $S = 1.038$

2904 reflections

354 parameters

H atoms riding

 $w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 5.4341P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.149$ $\Delta\rho_{\text{max}} = 1.118 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -1.128 \text{ e \AA}^{-3}$

Extinction correction:

SHELXTL

Extinction coefficient:

0.0024 (4)

Atomic scattering factors

from *International Tables*for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

Flack (1983)

Flack parameter = 0.11 (9)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ge1	0.23377 (13)	0.53455 (18)	0.30130 (10)	0.0240 (5)
Ge2	0.25244 (13)	0.57672 (19)	0.09496 (10)	0.0281 (5)
Ge3	0.47707 (14)	0.6085 (2)	0.25573 (11)	0.0364 (6)
S1	0.1671 (4)	0.3685 (4)	0.3581 (3)	0.0342 (10)
S2	0.2020 (4)	0.6962 (4)	0.3832 (3)	0.0381 (11)
S3	0.2360 (4)	0.3897 (5)	0.0302 (3)	0.0440 (12)
S4	0.1639 (4)	0.7117 (5)	-0.0054 (3)	0.0395 (11)
N1	0.1800 (10)	0.5521 (15)	0.1841 (8)	0.037 (4)
N2	0.3976 (11)	0.6198 (19)	0.1470 (9)	0.050 (5)
N3	0.3892 (10)	0.5247 (14)	0.3176 (7)	0.026 (3)
C1	0.1736 (15)	0.2270 (17)	0.2879 (11)	0.036 (4)
C1A	0.160 (2)	0.120 (2)	0.3460 (14)	0.065 (6)
C1B	0.076 (2)	0.238 (2)	0.204 (1)	0.058 (6)
C1C	0.287 (2)	0.220 (2)	0.261 (1)	0.051 (5)
C2	0.048 (1)	0.699 (2)	0.387 (1)	0.042 (5)
C2A	0.027 (2)	0.831 (2)	0.409 (2)	0.087 (10)
C2B	-0.025 (2)	0.662 (2)	0.298 (1)	0.062 (6)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ge1—N1	1.809 (12)	Ge2—S3	2.216 (5)
Ge1—N3	1.829 (12)	Ge3—N2	1.755 (13)
Ge1—S1	2.203 (4)	Ge3—N3	1.818 (12)
Ge1—S2	2.224 (4)	Ge3—S6	2.171 (4)
Ge2—N1	1.808 (14)	Ge3—S5'	2.188 (7)
Ge2—N2	1.821 (11)	Ge3—S6'	2.258 (7)
Ge2—S4	2.212 (5)	Ge3—S5	2.272 (5)
N1—Ge1—N3	105.4 (5)	N2—Ge3—S6	120.0 (5)
N1—Ge1—S1	114.3 (5)	N3—Ge3—S6	115.1 (4)
N3—Ge1—S1	110.5 (4)	N2—Ge3—S5'	129.1 (7)
N1—Ge1—S2	115.8 (5)	N3—Ge3—S5'	121.7 (5)
N3—Ge1—S2	105.4 (4)	N2—Ge3—S6'	82.3 (7)
S1—Ge1—S2	105.0 (2)	N3—Ge3—S6'	99.1 (6)
N2—Ge2—N1	105.7 (6)	S5'—Ge3—S6'	101.9 (5)
N2—Ge2—S4	114.6 (6)	N2—Ge3—S5	95.6 (7)
N1—Ge2—S4	113.6 (5)	N3—Ge3—S5	112.0 (5)
N2—Ge2—S3	114.2 (6)	S6—Ge3—S5	105.2 (2)
N1—Ge2—S3	102.3 (5)	Ge1—N1—Ge2	131.9 (7)
S4—Ge2—S3	106.1 (2)	Ge3—N2—Ge2	132.6 (8)
N2—Ge3—N3	107.1 (6)	Ge3—N3—Ge1	126.5 (7)

The two *tert*-butylthiolate groups bonded to the Ge3 atom are disordered and display alternate positions for the S and C atoms. The occupancy ratio is 3:1. Both the S and C atoms were refined with bond-distance restraints and the C atoms were refined with next nearest neighbor distance restraints. The displacement parameters for the lower occupancy C atoms were isotropic and fixed. Large difference peaks remain within the disordered *tert*-butyl groups indicating an additional level of disorder, however, it was not possible to model it discretely.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL (Sheldrick, 1994). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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[pyH⁺]₂[CdNb₂(py)₄O₂F₁₀]²⁻

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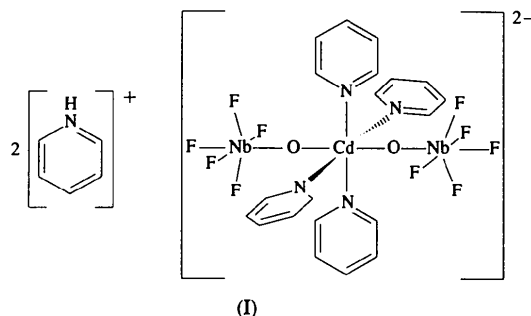
Abstract

A new Cd^{II}/Nb^V compound, bis(pyridinium) decafluoro-2κ⁵F₃κ⁵F-di-μ-oxo-1:2κ²O;1:3κ²O-tetrakis(pyridine-N)-cadmiumdiniobium(2-), (C₅H₆N)₂[CdNb₂F₁₀O₂(C₅H₅-N)₄], has been synthesized. The complex contains [CdNb₂(py)₄F₁₀O₂]²⁻ anions (py is pyridine) linked *via* the pyridinium cation through N—H⁺···F hydrogen bonding. The anion is composed of two [NbF₅O_{1/2}]⁻ octahedra connected by O²⁻ to a central [Cd(py)₄O_{2/2}]⁻ octahedron.

Comment

The new mixed metal compound, [pyH⁺]₂[CdNb₂(py)₄O₂F₁₀]²⁻, (I), is isostructural with [pyH⁺]₂[CuNb₂(py)₄O₂F₁₀]²⁻ (Halasyamani *et al.*, 1996). The title metal complex contains anionic [CdNb₂(py)₄O₂F₁₀]²⁻ clusters linked *via* the pyridinium cation through hydrogen bonding. Each cluster is composed of two [NbF₅O_{1/2}]⁻ octahedra connected through O²⁻ to a central [Cd(py)₄O_{2/2}]⁻

octahedron. The niobium cations are displaced from the center of the [NbF₅O_{1/2}]⁻ octahedra towards the bridging O atoms (Goodenough & Longo, 1970) in an anti-parallel manner.



Single crystal diffraction data revealed only three unique atoms in the asymmetric unit for pyridinium, indicating disorder. Owing to a number of possible disorder constraints, the probable N(3)—H⁺···F hydrogen-bonding interactions were used to disorder N(3) and C(9). Only one hydrogen-bonding interaction, however, occurs for each ring. The large *U*₃₃ value observed for the F(3) atom is due to the possible hydrogen-bonding interactions.

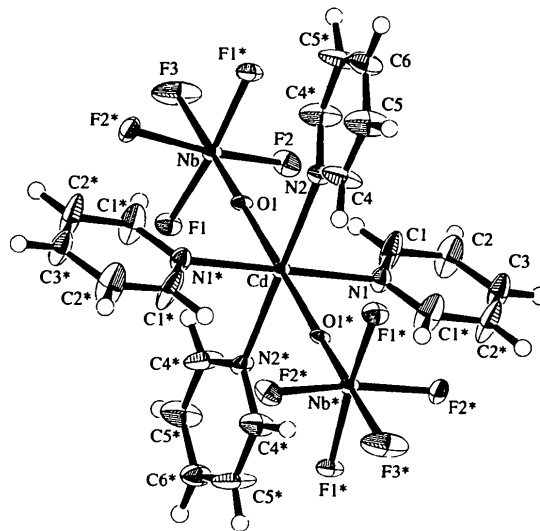


Fig. 1. ORTEP (Johnson, 1976) plot (50% probability ellipsoids) of the polynuclear anion [CdNb₂(py)₄O₂F₁₀]²⁻.

The bond lengths of (I) compare well with other compounds. For example, the Nb—O/F distances, Nb—F_{trans} 2.097 (6), Nb—O 1.747 (7) and Nb—F_{eq} 1.935 (4) Å, compare well to the Nb—O/F distances of Nb—F_{trans} 2.095 (2), Nb—O 1.765 (2) and Nb—F_{eq} 1.925 (2)–1.974 (2) Å in Na₂[NbF₅O] (Stomberg, 1983). In addition, the average Cd—N distance of 2.35 (1) Å is in good agreement with the Cd—N distance of 2.341 (5) Å in [Cd(NH₃)₄(I₂)₂] (Tebbe & Plewa, 1982).