

Letters to the Editor

Synthesis and structure of bis(acetylacetonato)germanium(IV) diazide

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We found that refluxing of $(\text{Acac})_2\text{GeCl}_2$ with NaN_3 (2 mol) in acetonitrile for 5 h gave bis(acetylacetonato)germanium(IV) diazide $(\text{Acac})_2\text{Ge}(\text{N}_3)_2$ (**1**) in an 82% yield. Complex **1** was isolated as colorless crystals well soluble in organic solvents and readily hydrolyzed in air.

Single crystals of **1** were obtained by recrystallization from toluene. At -110°C crystals **1** are monoclinic, space group *Cc*, $a = 9.199(2)$ Å, $b = 12.632(3)$ Å, $c = 12.532(3)$ Å, $\beta = 93.70(3)^\circ$, $Z = 4$, $V = 1453.3(5)$ Å³, $R_1 = 0.0320$, $wR_2 = 0.0716$. According to X-ray structural analysis, the Ge atom in complex **1** (Fig. 1) is in the distorted octahedral environment of four O atoms ($\text{Ge}-\text{O}(1)$ 1.891(9) Å, $\text{Ge}-\text{O}(2)$ 1.935(9) Å, $\text{Ge}-\text{O}(3)$ 1.889(9) Å, $\text{Ge}-\text{O}(4)$ 1.898(9) Å), two Acac ligands, and N atoms of two azide fragments ($\text{Ge}-\text{N}(1)$ 1.942(12) Å, $\text{Ge}-\text{N}(4)$ 1.926(11) Å) arranged in *cis*-position with respect to each other and in the axial and equatorial positions of complex **1**, respectively.

Compound **1** is the first structurally characterized azide-containing β -diketonate of the hexacoordinate atom of Group IVB elements of the Periodic System.

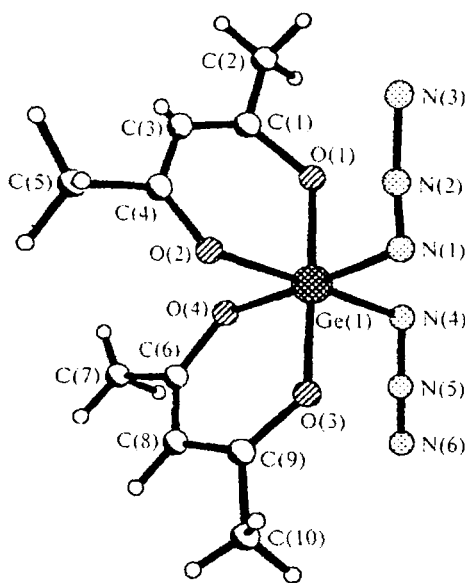


Fig. 1. Molecular structure of $(\text{Acac})_2\text{Ge}(\text{N}_3)_2$.

Since it is known that diazide-containing derivatives of Group IVB elements generate carbene analogs upon photolysis,^{1,2} we studied the photochemical decomposition of complex **1** in benzene (20 °C, 20 h, a DRSh-1000 high-pressure mercury lamp). However, a poorly soluble germanium-containing polymer is formed under these conditions instead of the expected germanium(II) bis(acetylacetonate).

Bis(acetylacetonato)germanium(IV) diazide (1). M.p. 136–137 °C. IR (KBr), ν/cm^{-1} : 1540 (C=O), 2113 (N_3). ^1H NMR: (C_6D_6), δ : 1.08 (s, 6 H, 2 CH_3); 1.13 (s, 6 H, 2 CH_3); 5.09 (s, 2 H, CH_2). MS (EI, 70 eV), m/z (I_{rel} (%)): 314 [$\text{M} - \text{N}_3$]⁺ (41), 272 [$\text{M} - 2 \text{N}_3$]⁺ (3.5), 257 [$\text{M} - \text{Acac}$]⁺ (17), 173 [$\text{M} - 2 \text{N}_3 - \text{Acac}$]⁺ (100).

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References

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