Characterization and X-Ray Crystal Structure of a Monomeric Germylene Derivative, Ge(acac)I (Hacac = Acetylacetone)

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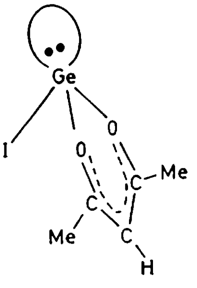
Summary The complex Ge(acac)I (Hacac = acetylacetone) has been characterized and its structure determined by a single-crystal X-ray structural analysis; the monomeric molecule is pyramidal with bond lengths Ge–I, 2·736(1) and Ge–O, 1·914(5) and 1·931(5) Å and bond angles O–Ge–O, 91·38(22) and I–Ge–O, 91·60(16) and 93·92(16)°.

Whereas derivatives of carbon(II) (*i.e.*, 'carbenes') are extremely reactive transient species, some germanium(II) analogues ('germylenes') are significantly more stable and can be isolated. Nevertheless, the chemistry of these compounds is not well developed and only two structural studies have previously appeared, both of adducts of germanium(II) chloride: an early study of $GeCl_2$(dioxan),[1] and a more recent report on the structure of $GeCl_2$(Benzthiazole).[2] Here we communicate the results of an X-ray structural investigation of a germanium(II) keto-enolato complex, Ge(acac)I (**1**) (Hacac = acetylacetone).[3]



(1)

Crystal data: $C_5H_7GeIO_2$, M 298·6, orthorhombic, space group *Pbca* (D_{2h}^{15}; No. 61), $a = 10{\cdot}5504(17)$, $b = 14{\cdot}0729(23)$, $c = 11{\cdot}5336(18)$ Å, $U = 1712{\cdot}4(5)$ Å^3, $D_c = 2{\cdot}32$ g cm^{-3}, $Z = 8$, μ(Mo-K_α) = 73·6 cm^{-1}.

A translucent lemon-yellow crystal was sealed (under air- and moisture-free conditions) into a capillary and diffraction data were collected with a Syntex $P2_1$ automated four-circle diffractometer using a coupled θ(crystal)–2θ(counter) scan technique[4] and graphite-monochromatized Mo-K_α radiation. Data were corrected for absorption by an empirical method based upon a series of ψ-scans of close-to-axial reflections.[5] The structure was solved by a combination of Patterson and difference-Fourier methods and the structure was refined by full-matrix least-squares using our in-house Syntex XTL system. All atoms (including all hydrogen atoms) were located and refined (anisotropically for non-hydrogen atoms; isotropically for hydrogens).

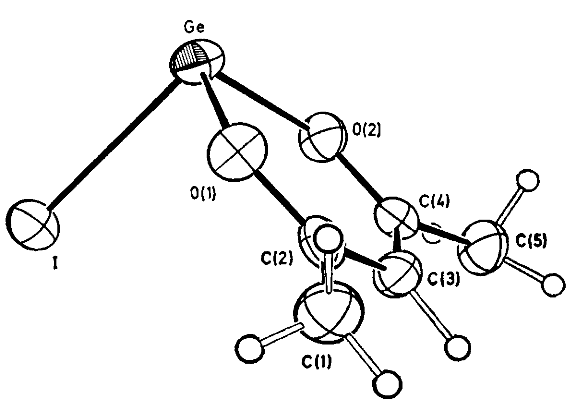


Figure. The structure of Ge(acac)I (**1**).

Convergence was reached with R 5·9% for all 1113 independent data with $4{\cdot}0° < 2\theta < 45°$ (not one datum rejected). The resulting structure for the complex (**1**) is shown in the Figure.†

Compound (**1**) is monomeric and three-co-ordinate about the central germanium atom with distances Ge–I, 2·736(1); Ge–O(1), 1·931(5); and Ge–O(2), 1·914(5) Å. Although this leads to an exposed metal centre, its closest intermolecular contacts are Ge · · · I($-x, -y, -z$), 3·754(1) and Ge · · · I($-1/2 + x, y, 1/2 - z$), 3·820(1) Å. The resulting pyramidal co-ordination environment corresponds to a three-bonding pair–one lone pair valence shell for the Ge^{II} atom; angles around the latter are as follows: I–Ge–O(1), 91·60(16); I–Ge–O(2), 93·92(16); and O(1)–Ge–O(2), 91·38(22)°. Distances within the acetylacetonato ligand are symmetrical with (cyclically) O(1)–C(2), 1·297(11); C(2)–C(3), 1·365(12); C(3)–C(4), 1·359(13); and C(4)–O(2), 1·299(10) Å; the two C–Me linkages are C(2)–C(1), 1·490(14) and C(4)–C(5), 1·489(14) Å, while C–H distances average 1·02 Å. The molecule approximates to C_s symmetry and the O(1)–C(2)–C(3)–C(4)–O(2) system has a root-mean-square deviation from planarity of 0·025 Å; the germanium(II) atom lies 0·089 Å from this plane.

The unassociated character of complex (**1**) contrasts with the situation found for $Sn(C_5H_5)Cl$ which exhibits unsymmetrical intermolecular bridging through chlorine in the crystal.[6] Lewis-base properties corresponding to the obvious stereochemical influence of the non-bonding electron pair in complex (**1**) have been identified in related compounds for example $Ge(C_5H_4Me)_2$ which readily[7] forms an adduct with BF_3.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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