Chemistry of Bulky Alkoxides of Bivalent Germanium and Tin; Structures of Gaseous $[Sn(OBu^t)_2]_2$ and Crystalline $Ge(OCBu^t{}_3)_2$†

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Structural studies of bulky group 4B metal(II) alkoxides reveal that (i) gaseous tin(II) t-butoxide, (**1**), is the *trans*-dimer with a remarkably small endocyclic OSnO angle of 76(2)°, (ii) the crystalline (tri-t-butyl)methoxides of Ge^{II}, (**2a**), and Sn^{II}, (**2b**), are isomorphous V-shaped monomers, with an exceptionally small OGeO angle in (**2a**) of 85.9(4)°, and (iii) the ^{119}Sn n.m.r. chemical shifts in C_6D_6 are distinct for alkoxides in which tin has co-ordination number of two (**2b**), three (**1**), or four $[SnI(Me)(OCBu^t{}_3)_2]$.

Only an isolated observation has been made on the structure of a Sn^{II} alkoxide: Veith and Töllner having recently shown, by variable temperature ^1H n.m.r. spectroscopy and cryoscopy, that the t-butoxide is dimeric in benzene, (**1**); however from its volatility (sublimation at *ca.* 60 °C/10^{-3} Torr) and mass spectrum they inferred that in the vapour it is a monomer.[1]

We now report some structural data on Ge^{II} and Sn^{II} alkoxides for crystalline (*X*-ray), solution (^{119}Sn n.m.r.), and vapour [gas-phase electron diffraction (g.e.d.)] phases. The compounds described are $[Sn(OBu^t)(\mu\text{-}OBu^t)]_2$, (**1**), $M(OCBu^t{}_3)_2$, (**2a**; M = Ge) and (**2b**; M = Sn), and $SnI(Me)(OCBu^t{}_3)_2$, (**3**).

The syntheses of the *colourless* compounds (**1**)—(**3**) are illustrated in Scheme 1; we draw particular attention to the ^{119}Sn n.m.r. data on the three tin alkoxides in which the co-ordination number of the tin is 2 (**2b**), 3 (**1**), or 4 (**3**).

G.e.d. results (for experimental details, see ref. 2) on bis(t-butoxy)tin(II) vapour at a nozzle temperature of *ca.* 385 K are consistent with a model consisting only of dimers

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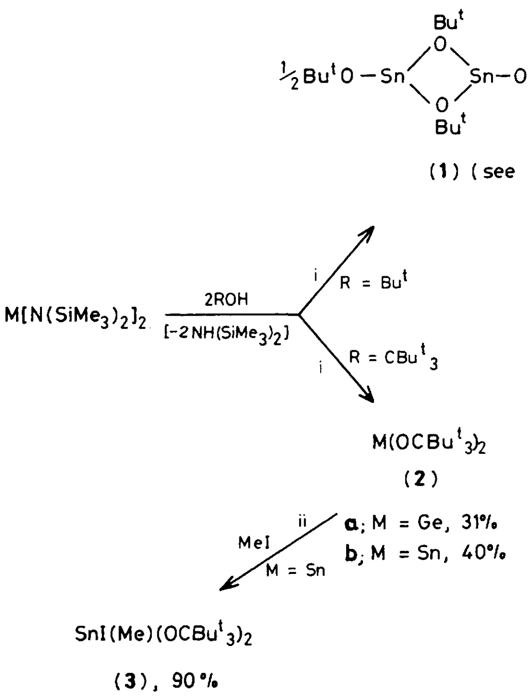
† No reprints available.



Scheme 1. *Reaction conditions:* i, n-C_6H_{14}, *ca.* 25 °C [(**1**) (5 min) or (**2a**) (2 days)] or 2 weeks at −25 °C (**2b**); ii, MeI as solvent, 2 weeks −60 to +30 °C. *Identification:* compounds (**2a**) and (**2b**) were obtained as colourless cubes from PhMe at −30 °C (*X*-ray data in Figure 2); they and (**3**) were characterised by microanalysis, ^1H, ^{13}C, and except for (**2a**), ^{119}Sn n.m.r. [δ (p.p.m.) rel. to $SnMe_4$: (**1**), −93.6; (**2b**), −162.9; (**3**), −395 {centre of quartet, $^2J(^{119}SnC^1H)$ 90 Hz}]; g.e.d. data for (**1**) are summarised in Figure 1.

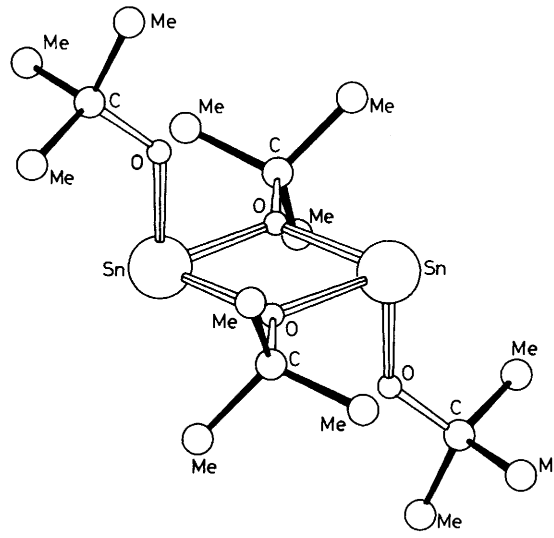


Figure 1. Molecular model of $[Sn(\mu\text{-}OBu^t)(OBu^t)]_2$, (**1**), as determined by g.e.d. (b = bridge, t = terminal). Selected bond lengths (Å) and angles (°): <Sn–O_b> 2.16(1), <Sn–O_t> 1.97(2), <C–O> 1.41(2), <C–C> 1.55(1) Å; O_b–Sn–O_b 76(2), Sn–O_b–Sn 104(2), Sn–O_b–C 127(2), Sn–O_t–C 132(2)°. The Sn–O_t bonds are nearly perpendicular to the Sn · · · Sn vector [Sn · · · Sn 3.40(3) Å].

(**1**) of C_i symmetry, although small percentages of monomers or other species cannot be excluded. Key dimensions of the assumed planar four-membered $(SnO)_2$ ring and its pendant groups are indicated in Figure 1. Among the noteworthy features are (a) the *trans*-arrangement of the terminal OBu^t groups, (b) the nearly planar environment of the bridging O's [Σ of angles at O_b = 358(2)°], and (c) the strained geometry at each Sn. Thus it is evident that lone pairs may be stereochemically inactive (O_b) [see (b)] or active (Sn) [see (c)]. The co-ordination geometry of tin in (**1**) has a single precedent; crystalline $[Sn(\mu\text{-}NMe_2)(NMe_2)]_2$ has an N_bSnN_b angle of 80.0(1)°.[3]

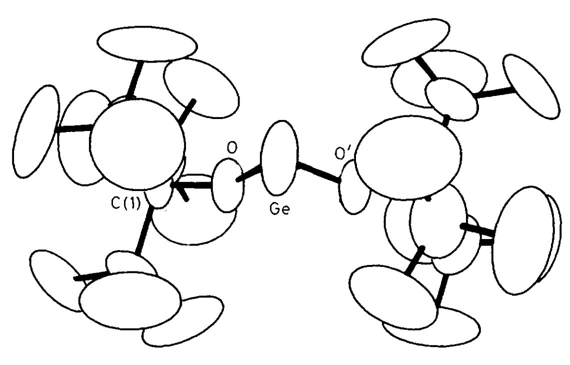


Figure 2. An ORTEP drawing of $Ge(OCBu^t_3)_2$, (**2a**), with atoms shown as 50% thermal vibration ellipsoids. Only one of the six equivalent Ge sites is shown. Relevant dimensions are: Ge–O 1.896(6), Ge–O' 1.832(11), C(1)–O 1.41(1) Å; O–Ge–O' 85.9(4), C(1)–O–Ge 131.9(5), C(1')–O'–Ge 134.0(7)°. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The bulky $^-OCBu^t_3$ ligand [as in (**2**) and (**3**)] was recently introduced by Power and co-workers, who reported on the structures of Li^+, Cr^{II}, and Mn^{II} alkoxides;[4] extensions to Ti^{IV} and Zr^{IV} compounds have been published.[5] The molecule (**2a**) (Figure 2) lies on a site of crystallographic $\bar{3}$ symmetry with the Ge atom disordered over six equivalent sites. *Crystal data* for (**2a**): $C_{26}H_{54}O_2Ge$, M = 471.3, cubic, space group $Pa3$, a = 14.015(6) Å, U = 2752.8 Å^3, Z = 4, D_c = 1.14 g cm^{-3}. [Compound (**2b**) is isomorphous, with a = 14.152(8) Å.] There are very large thermal vibrational parameters for the t-butyl group atoms and a limited data set of 228 reflections [$I > \sigma(I)$, CAD4 diffractometer, Mo-K_α radiation] has been obtained, with R = 0.11 after least-squares refinement. The Ge–O bonds average 1.87(4) Å.

The sole previous structure determinations of alkoxides of Sn or Ge concern $Sn(OMe)_3Me$, having an infinite $-(O\text{–}Sn\text{–})_\infty$ chain,[6] $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OMe)_4$,[7] $Sn(\mu_2\text{-}OBu^t)_3Tl$ [<Sn–O> 2.023(9) Å],[8] $[SnCl_3(EtOH)(\mu_2\text{-}OEt)]_2$ [<Sn–OEt> 2.09(3) Å],[9] a porphinato-Ge^{IV}-$(OMe)_2$ [<Ge–O> 1.822(3) Å],[10] and $Ge[CH(SiMe_3)_2]_2H(OEt)$ [Ge–O 1.797(5) Å].[11]

Monomeric Ge^{II} and Sn^{II} compounds MX_2 where X^- is a monohapto ligand, all of which have been *coloured*, are rare, being at present established in the crystal only for a handful of compounds: X = $N(SiMe_3)_2$,[12] $\overline{NCMe_2(CH_2)_3CMe_2}$,[13] OAr (Ar = $C_6H_2Me\text{-}4\text{-}Bu^t_2\text{-}2,6$),[14] or SAr' (Ar' = $C_6H_2Bu^t_3\text{-}2,4,6$),[15] and additionally[16] in the vapour for X = $CH(SiMe_3)_2$ ($X_2M{=}MX_2$ in the crystal). A curiosity has been the wide variation in the XMX angle: from 85.4(1)° in $Sn(SAr')_2$[15] to 111.4(5)° in $Ge[\overline{NCMe_2(CH_2)_3CMe_2}]_2$.[13] Small XMX angles are surprising, not only because the ligands X^- are bulky, but also because the lower limit might have been expected to be 90° (representing pure p_xp_y orbitals).

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