Metal (Li, Ge^{II}, Ge^{III}, Sn^{II}, and Pb^{II}) 2,6-Dialkylbenzenethiolates; X-Ray Crystal Structures of Sn(SAr)$_2$ (Ar = C$_6$H$_2$Bu$^t_3$-2,4,6) and [M(SAr')$_2$]$_3$ (M = Sn or Pb, Ar' = C$_6$H$_3$Pr$^i_2$-2,6)†

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Complexes [Li(SAr)(OEt$_2$)]$_n$, M(SAr)$_2$ [Ar = C$_6$H$_2$Bu$^t_3$-2,4,6; M = Ge, Sn (**3b**), or Pb], [Cr(CO)$_5${Sn(SAr)$_2$}], Sn(I)(Me)(SAr)$_2$, ·Ge(SAr)$_3$ (**7a**), and [M(SAr')$_2$]$_3$ [Ar' = C$_6$H$_3$Pr$^i_2$-2,6; M = Sn (**8a**) or Pb (**8b**)] are hydrocarbon-soluble and crystalline [except for the transient (**7a**)]; X-ray structures of the title complexes (**3b**) [a V-shaped monomer with an SSnS angle of 85.4(1)° and Sn–S$_{av}$ 2.435(1) Å] and (**8**) [M(SAr')(μ-SAr')$_2$M(μ-SAr')$_2$M(SAr')] reveal metal co-ordination numbers of 2 for the former or 3, M(terminal) and 4, M(central) for the latter, Sn–S$_t$ 2.471(5), mean Sn–S$_{br}$ 2.66(10), Pb–S$_t$ 2.554(4), and mean Pb–S$_{br}$ 2.76(9) Å.

We report the first examples of metal benzenethiolates bearing bulky substituents in the *o*- and *o'*-positions, see Scheme 1, for complexes derived from ArSH (Ar = C$_6$H$_2$Bu$^t_3$-2,4,6), (**1**),[1] and Ar'SH (Ar' = C$_6$H$_3$Pr$^i_2$-2,6), (**2**).[2]

The 2,6-dialkylbenzenethiolate ligands ArS$^-$ and Ar'S$^-$ are of interest because of (i) their conferment of lipophilicity on their metal complexes [*n.b.*, each of (**1**)—(**8**) is hydrocarbon soluble], (ii) their potential for stabilisation of unusual metal valence states (here Ge^{II}, Sn^{II}, Pb^{II}; and, to some

extent Ge^{III}), co-ordination numbers [now 2, for complexes (**3**), or 3, for complexes (**5**), (**7a**), and (**8**)], or other features of molecular structure [*cf.*, the unprecedented linear trimeric structures of complexes (**8**), Figure 1], and (iii) their widespread capacity for functioning as terminal ligands. The present studies are complementary to others dealing with complexes having ArO$^-$,[3] NHAr,[4] or Ar$^-$[5] ligands.

The Sn^{II} thiolate Sn(SAr)$_2$, (**3b**), differs from other SnX$_2$ molecules [which are monomers in solution, *e.g.*, X = CH(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$, or OAr] in being a potentially ambidentate nucleophile [but like these, and its Ge^{II} and Pb^{II} analogues, (**3a**) and (**3c**), is thermochromic, becoming redder
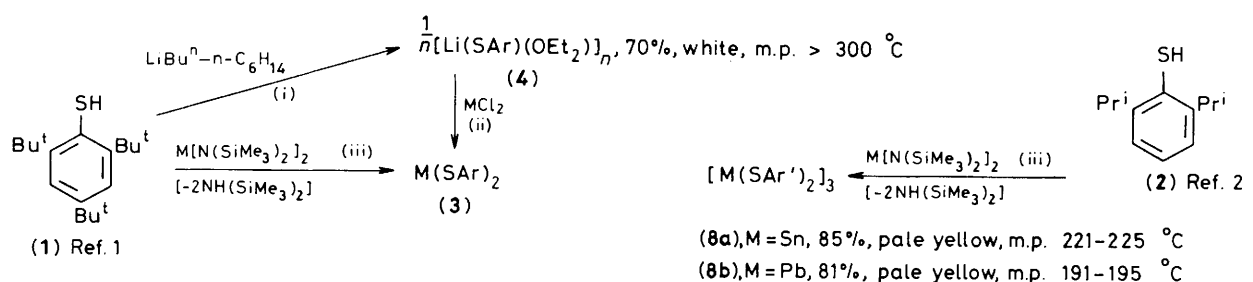
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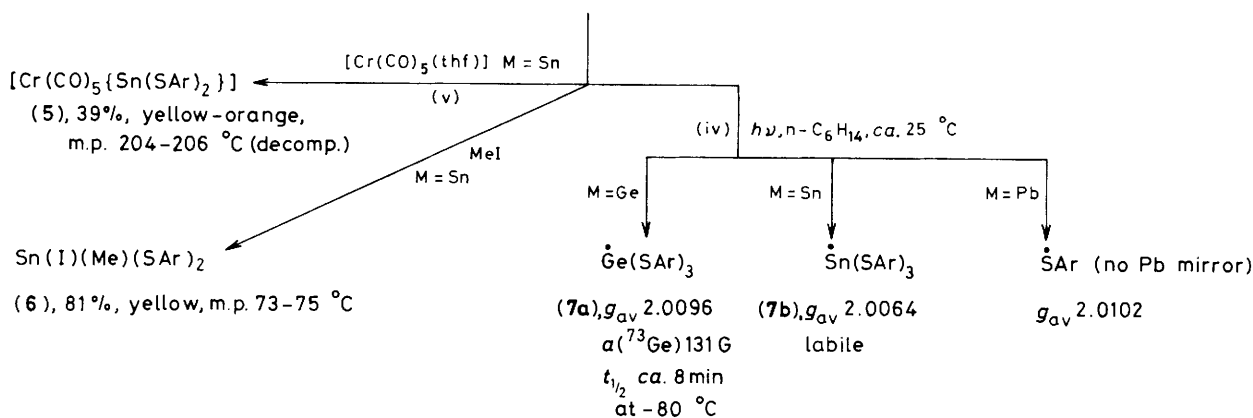
Scheme 1. *Reaction conditions:* (i) OEt_2, *ca.* 25 °C, $2\frac{1}{2}$ h, then -30 °C and filter; (ii) $GeCl_2$–dioxane or $SnCl_2$, *ca.* 25 °C, 72 h, then successive removal of OEt_2, extraction into n-C_5H_{12} (Ge) or n-C_6H_{14}, cooling (-30 °C), and filtering; (iii) n-C_5H_{12}, 12 h, then successive concentration, cooling (-30 °C) and filtering; (iv) $h\nu$, n-C_6H_{14}, *ca.* 25 °C; (v) OEt_2, *ca.* 25 °C, 12 h, then successive filtration, removal of OEt_2 from filtrate, extraction into PhMe, cooling (-30 °C), and filtering. *Characterisation:* crystalline compounds (2)—(6) and (8) were analytically pure and gave satisfactory i.r., [1]H n.m.r., and [13]C n.m.r. spectra.

on heating]. However, ^{1}H and [119]Sn n.m.r. evidence suggests that in $Sn(I)(Me)(SAr)_2$, (6), it is the Sn rather than a S atom which is the donor site. In complex (5) Cr–Sn bonding may be assumed by analogy with the X-ray authenticated $[Cr(CO)_5\{Ge(SC_6H_2Me_3\text{-}2,4,6)_2\}]$.[6]

The radical ·$Ge(SAr)_3$, (7a), was unambiguously characterised when the irradiation [(iv) in Scheme 1] was carried out at -80 °C in the cavity of an e.s.r. spectrometer. The corresponding experiment with $Sn(SAr)_2$, (3b), probably yields the labile ·$Sn(SAr)_3$, (7b), but [119]Sn hyperfine coupling was not observed. The far greater lability of the radicals (7) compared with certain ·MX_3 analogues [*e.g.*, X = $CH(SiMe_3)_2$ or $N(SiMe_3)_2$],[7] is unexpected.

In $[M(SAr')_2]_3$, (8), the terminal M atoms may be regarded as having tetrahedral geometry with one lone pair, while the central M has distorted trigonal bipyramidal geometry with an equatorial lone pair, Figure 1. There are two M_2S_2 rings related by a crystallographic two-fold axis through M(1), each with the Ar' groups on the bridging S atoms on one side of the ring and the terminal SAr' group on the other side of the ring, presumably for steric reasons. The bonds from M(2) to the terminal SAr' are slightly shorter than those to the bridging SAr', and for the central metal atom, the M(1)–S(2) axial bonds are significantly longer than the M(1)–S(1) equatorial bonds. For the central metal atom, S(ax.)–M–S(ax.) angles of 147 for Pb and 145° for Sn are larger than the equivalent angles (140 and 133°) in the otherwise similar monomeric complexes $[Pb(S_2CNEt_2)_2]$[8] and $[Sn(S_2CNEt_2)_2]$,[9]

presumably owing to constraints arising from the bite angles of the chelating S atoms of the dithiocarbamates.

A comparison of bond lengths and bond angles in the Sn and the Pb trimers (8a) and (8b) shows an increase for the latter in (i) the M–S bond lengths of between 0.06 and 0.14 Å and (ii) the angles S(1)–M–S(1') and S(2)–M–S(2') (by 3.3 and 1.9°, respectively). However the main difference seems to lie in the orientation of the aryl groups on S(1) and S(3) where the respective torsion angles for the Sn and Pb complexes are M(2)–S(3)–C(13)–C(14) 89 and 76°, S(1)–M(2)–S(3)–C(13) -139 and $-128°$, and M(1)–S(1)–C(1)–C(2) -71 and $-64°$.

In contrast, $Sn(SAr)_2$, (3b), is monomeric, Figure 2. It lies on the crystallographic two-fold axis and the shortest Sn $\cdots$ S intermolecular contacts are with the next molecule one unit cell away up the two fold axis, at 4.4 Å, not significantly shorter than the normal van der Waals contacts. The S–Sn–S angle of 85.4(1)° is remarkably small, less than that found in crystalline $Sn(OAr)_2$, 88.8(2)[10] or $[Sn\{N(SiMe_3)_2\}_2]$, 104.7(2)°,[11] and is therefore probably not due to a steric effect.

Crystal data:‡ $C_{72}H_{102}S_6Sn_3$, (8a), and [in brackets] $C_{72}H_{102}Pb_3S_6$, (8b): $M = 1516.1$ [1781.6], monoclinic, space

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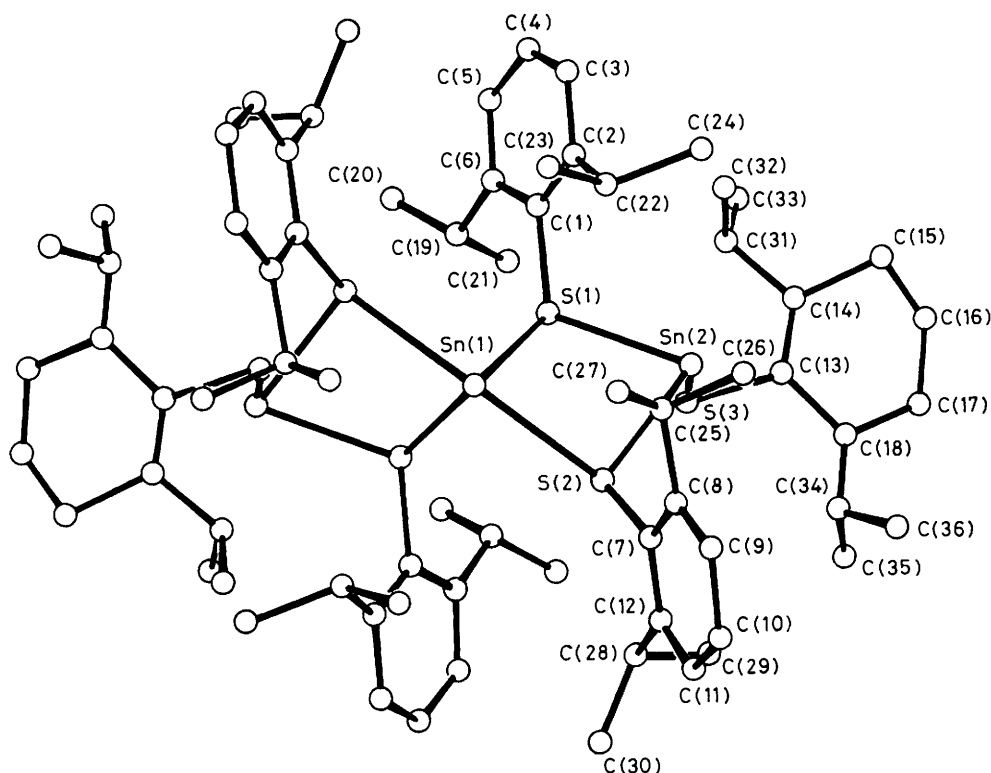
Figure 1. The molecular structures and atom numbering schemes for [M(SAr′)₂]₃, (8). Relevant dimensions for M = Sn, (8a) [M = Pb, (8b), in brackets] are: Sn(1)–S(1) 2.588(4) [2.680(3)], Sn(1)–S(2) 2.838(4) [2.896(3)], Sn(2)–S(1) 2.643(4) [2.780(3)], Sn(2)–S(2) 2.583(4) [2.673(3)], Sn(2)–S(3) 2.471(5) [2.554(4)] Å; S(1)–Sn(1)–S(1′) 86.0(2) [89.3(2)], S(2)–Sn(1)–S(2′) 145.2(2) [147.1(1)], S(1)–Sn(1)–S(2) 71.1(1) [71.5(1)], S(1)–Sn(2)–S(2) 74.4(1) [73.5(1)], S(1)–Sn(2)–S(3) 89.8(2) [92.8(1)], S(2)–Sn(2)–S(3) 95.0(1) [92.6(1)]°.
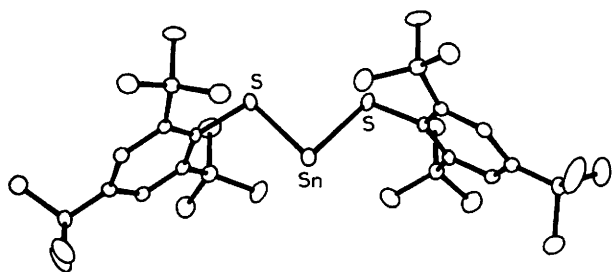
Figure 2. The molecular structure of Sn(SAr)₂, (3b): Sn–S 2.435(1) Å, S–Sn–S 85.4(1)°.

group C2 [C2/c], a = 24.796(4) [25.287(9)], b = 10.850(6) [10.761(4)], c = 17.095(2) [31.364(3)] Å, β = 116.84(1) [105.94(2)]°, Z = 2 [4], R = 0.066 [0.066], R′ = 0.099 [0.099] for 1749 [2972] unique reflections in the range 2 < θ < 20°. Compounds (8a) and (8b) are *not* isostructural. C₃₆H₅₈S₂Sn, (3b), M = 673.7, orthorhombic, space group Fdd2, a = 19.864(3), b = 63.336(11), c = 5.860(1) Å, Z = 8, R = 0.036, R′ = 0.049 for 1605 unique reflections in the range 2 < θ < 25°.

Data were measured on an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-K_α radiation. For structures (8a) and (8b), the Sn, Pb, and S atoms were refined anisotropically, and for (3b), this was also the case for the C atoms.

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