

the best plane are in the range of -0.022 (4) [O(1)] to 0.016 (1) Å (Ni). The phenyl ring is planar with the value of χ^2 (0.05, 3) = 6.6. The torsion angles N(1)–C(1)–C(2)–N(2) and N(2)–C(3)–C(4)–N(3) are 50 and -42° respectively. From the above planes, the largest dihedral angle of 12.9° is between the phenyl and the Ni–N(2)–C(3)–C(4)–N(3) planes.

The perchlorate anion is disordered. The maxima of the electron density related to the O atoms of the perchlorate anion were interpreted as two perchlorate anions with one shared Cl–O(2) bond and with occupancy factors of 0.5 for the O atoms O(31), O(32), O(41), O(42), and O(51), O(52) respectively. From a number of perchlorate locations tried, this model led to the best *R*-factor value. The large thermal parameters of O(Cl) atoms and the allocation of the maxima and minima in the $\Delta\rho$ map to these atoms shows that the perchlorate anion may rotate along the Cl–O(2) bond. This is in accordance with the fact that the ν_3 and ν_4

bands (1085 and 620 cm^{-1} respectively) in the infrared spectrum are not split.

An inspection of the crystal packing shows that the bonding of the complex cations and the perchlorate anions is predominantly ionic. The shortest intermolecular contacts are Ni \cdots O(32) = 3.20 (1), N(1) \cdots O(2ⁱ) = 3.18 (1) and N(1) \cdots O(51ⁱ) = 3.25 (2) Å ($i = -x, 0.5+y, 1.5-z$).

Dr V. Haber is thanked for providing the crystals.

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Dibutyldichlorotin(IV)

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Abstract. [SnCl₂(C₄H₉)₂], $M_r = 303.8$, monoclinic, *C2/c*, $a = 14.071$ (6), $b = 9.418$ (8), $c = 19.836$ (11) Å, $\beta = 103.78$ (4)°, $V = 2553$ (5) Å³, $Z = 8$, $D_x = 1.58\text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 23.9\text{ cm}^{-1}$, $F(000) = 1200$, $T = 298\text{ K}$, $R = 0.070$ for 1163 reflections with $I \geq 3\sigma(I)$. In the lattice, molecules of Bu₂SnCl₂ form polymeric chains *via* asymmetric Sn–Cl \cdots Sn bridges which are bent at Cl [Sn–Cl \cdots Sn = 104.3 (1), 104.8 (1)°] and nearly linear at Sn [Cl \cdots Sn–Cl = 172.3 (1), 173.1 (1)°]. Overall the geometry at Sn is distorted octahedral with C–Sn–C, Cl–Sn–Cl and $\langle\text{Cl–Sn–C}\rangle$ angles of 132.1 (7), 97.2 (2) and 105.6 (4)°, respectively. The primary Sn–Cl and secondary Sn \cdots Cl distances are 2.372 (5) and 2.388 (5) Å and 3.544 (5) and 3.514 (5) Å, respectively. The observed CSnC angle is significantly larger than that predicted by NMR data for Bu₂SnCl₂ in solution but is comparable to that observed in Et₂SnCl₂ and related molecules.

Introduction. The discussion concerning the degree of association, the nature of the intra- or intermolecular interactions or secondary bonding and the influence of

these interactions on the primary geometry of the Sn^{IV} atoms in the crystal structures of several diorgano- or triorganotin(IV) halides, $R_2\text{SnX}_2$ or $R_3\text{SnX}$ continues unabated (see, for example, Alcock & Sawyer, 1977; Amini, Holt & Zuckerman, 1987; Baxter, Holt & Zuckerman, 1985; Ganis, Valle, Furlani & Tagliavini, 1986; Lefferts, Molloy, Hossain, van der Helm & Zuckerman, 1982; Molloy, Quill & Nowell, 1985). Moreover, some correlations between intramolecular and intermolecular parameters by the use of the structure correlation method on data for Sn^{IV} compounds in the Cambridge Structural Database have been reported (Britton & Dunitz, 1981) and recently some evidence for molecular association in Me₂SnCl₂ has been presented using IR-band frequency shifts as a function of temperature (Herber, 1985). Similarly a very recent comparison of the solid-state and solution NMR structures of Me₂SnCl₂ (Lockhart & Farlee, 1987) has indicated that there is a small but significant change in the structure arising from solid-state effects (most notably in a change in the Me–Sn–Me angle of $\approx 6^\circ$). The present structure was determined in order to provide further data for these discussions, par-

ticularly since a ^{13}C and ^{119}Sn NMR study of Bu_2SnCl_2 in solution indicated that it had a CSnC angle of only 117° (Holeček, Nádvořník, Handlř & Lyčka, 1986), significantly less than the CSnC angle of $134.0(6)^\circ$ observed in the crystal structure of Et_2SnCl_2 (Alcock & Sawyer, 1977).

Experimental. Needle-shaped crystals (Alfa) selected and sealed in Lindemann capillaries under nitrogen. Long needle, described by the faces $\{0,1,0\}$, $\{1,0,0\}$ and $\{0,0,1\}$ which were 0.20, 0.015 and 0.015 cm respectively from an origin within the crystal, was used throughout. Peak profiles somewhat broad due to both crystal quality and the large b dimension of the crystal. Unit-cell dimensions were obtained by least-squares fit of the diffracting positions of 25 reflections ($11.6 < \theta < 16.1^\circ$) on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation. Intensity data collected using ω - 2θ scans over ω -scan ranges $(1.2 + 0.35 \tan \theta)^\circ$. Scan rates conditional on information collected in prescans (at $10^\circ \text{ min}^{-1}$) selected to give $I/\sigma(I) \geq 25$ within a max. scan time of 65 s. Three standard reflections monitored every 7500 s of exposure time showed no significant losses in intensity over data-collection period. Backgrounds by extending scan by 25% on either side of peak were measured for half the time taken to collect the peak. A few low-angle hkl data with $h + k = 2n + 1$ appeared to be weakly observed. All (5119, including standards) $h, k, \pm l$ data with $2\theta \leq 50^\circ$ measured ($h_{\text{max}} = 16, k_{\text{max}} = 11, |l|_{\text{max}} = 22$). Lorentz, polarization and absorption [*ABSCOR*, *SDP* package (Frenz, 1981): $6 \times 12 \times 6$ grid, min. T : 0.45, max. T : 0.56] corrections applied to all data. The few observed non- C -centred data were found to be between intense reflections and the space group was correctly assumed to be Cc or $C2/c$. Rejection of 169 standards and 3047 data which were systematically absent or had $F_{\text{obs}} = 0.0$ followed by averaging of 65 symmetry-equivalent data [$R_{\text{int}}(F) = 0.018$] gave a final data set of 1838 reflections.

Structure solution: Patterson, least-squares, Fourier and ΔF Fourier calculations. Large temperature factors for the outer C atoms in both butyl groups [especially C(1-4)] have distorted the geometries of these groups and prevented anisotropic refinement of the C atoms or location of the H atoms (12% of the electron density). Final least-squares refinement minimizing $\sum w\Delta F^2$ (Sn + Cl anisotropic) then converged (max. $\Delta/\sigma = 0.02$) to final agreement indices $R = 0.070$ ($wR = 0.112$) for 1163 observed data with $I \geq 3\sigma(I)$. Weights given by $w = 4F^2[\sigma^2(I) + (0.19F^2)^2]^{-1}$ and, at convergence, S was 1.085. Most significant features in a final ΔF map were some peaks up to $1.8 \text{ e } \text{Å}^{-3}$ in height near Sn. Programs: Enraf-Nonius *SDP* package (Frenz, 1981) on a PDP 11/23 computer. Atomic scattering factors stored in the programs were from *International Tables for X-ray Crystallography* (1974).

The final atomic positional and isotropic thermal parameters and bond lengths/bond angles are given in Tables 1 and 2.*

* Lists of structure-factor amplitudes and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44636 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic positional ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$)

	x	y	z	B_{eq} or B (Å^2)
Sn	2631.5 (7)	1321.3 (9)	2568.6 (5)	5.88 (2)*
Cl(1)	3631 (3)	3202 (5)	3137 (3)	8.2 (1)*
Cl(2)	3636 (3)	-590 (5)	3121 (2)	8.0 (1)*
C(1)	2761 (12)	1332 (14)	1529 (8)	6.8 (3)
C(2)	3769 (20)	1261 (20)	1440 (13)	12.6 (8)
C(3)	3815 (28)	1683 (33)	578 (20)	20 (1)
C(4)	3750 (32)	704 (40)	405 (23)	23 (1)
C(5)	1388 (11)	1317 (13)	3010 (8)	6.4 (3)
C(6)	1633 (13)	1260 (16)	3799 (10)	8.5 (5)
C(7)	718 (16)	1244 (20)	4055 (12)	11.2 (7)
C(8)	1069 (22)	1308 (22)	4843 (15)	13.5 (9)

Starred atoms were refined anisotropically: $B_{\text{eq}} = \frac{1}{3} \text{trace } \mathbf{B}$.

Table 2. Bond lengths (Å), bond angles ($^\circ$) and secondary-bond lengths (Å)

Sn-Cl(1)	2.372 (5)	C(1)-C(2)	1.47 (4)
-Cl(2)	2.388 (5)	C(2)-C(3)	1.77 (6)
-Cl(1')	3.544 (5)	C(3)-C(4)	0.98 (8)
-Cl(2'')	3.514 (5)	C(5)-C(6)	1.52 (3)
-C(1)	2.113 (17)	C(6)-C(7)	1.49 (3)
-C(5)	2.135 (16)	C(7)-C(8)	1.52 (4)
Cl(1)-Sn-Cl(2)	97.2 (3)	Cl(2'')-Sn-C(1)	76.7 (4)
-Cl(1')	172.3 (1)	-C(5)	76.8 (4)
-Cl(2'')	75.9 (1)	C(1)-Sn-C(5)	132.1 (7)
-C(1)	106.3 (4)	Sn-C(1)-C(2)	115 (2)
-C(5)	104.9 (4)	C(1)-C(2)-C(3)	111 (2)
Cl(2)-Sn-Cl(1')	75.1 (1)	C(2)-C(3)-C(4)	96 (6)
-Cl(2'')	173.1 (1)	Sn-C(5)-C(6)	115 (1)
-C(1)	105.8 (4)	C(5)-C(6)-C(7)	110 (2)
-C(5)	105.3 (4)	C(6)-C(7)-C(8)	105 (2)
Cl(1')-Sn-Cl(2'')	111.9 (1)		
-C(1)	76.7 (4)		
-C(5)	77.2 (4)		

Symmetry operations: (i) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

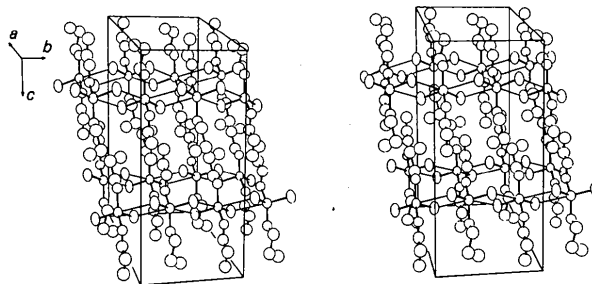


Fig. 1. Stereoscopic view approximately down a of the crystal packing in Bu_2SnCl_2 , showing the polymeric chains of interacting molecules. Secondary bonds are indicated by the thinner bonds.

Table 3. Selected features in the crystal packing of diorganodichlorotin compounds ($R_2\text{SnCl}_2$ except MePhSnCl_2)

	$R = \text{Me}$	Et	Bu	Me/Ph		Cx (I)	Cx (II)	Ph	
Overall CN of Sn	6	6	6	6 [Sn(1)]	5 [Sn(2)]	5 ^a	5 ^b	5 [Sn(1)]	6 [Sn(2)]
Sn—Cl (Å)	2.40 (4)	2.385 (4)	2.372 (5)	2.39 (1)	2.36 (1)	2.400 (5)	2.407 (2)	2.353 (2)	2.357 (2)
Shortest Sn...Cl (Å)	3.54 (5)	3.483 (4)	3.514 (5)	3.422 (9)	3.81 (1)	3.54	3.332 (2)	3.872	3.780
ClSnCl (°)	93 (2)	96.0 (1)	97.2 (2)	98.6 (3)	98.6 (3)	96.8 (2)	94.3 (1)	101.7 (1)	97.8 (1)
CSnC (°)	124 (4)	134.0 (6)	132.1 (7)	133 (1)	130 (2)	131.0 (9)	134.4 (2)	123.9 (2)	127.0 (2)

Notes: (a) $\text{Cl}(1)\text{Sn}\cdots\text{Cl}(2^i)$ as axial system (space group $P2_12_12_1$). (b) $\text{Cl}(1)\text{Sn}\cdots\text{Cl}(1^i)$ as axial system (space group $Pbcm$).

Discussion. In the lattice, molecules of Bu_2SnCl_2 form polymeric chains along the **b** direction *via* asymmetric Sn—Cl...Sn bridging interactions which are bent at Cl [Sn—Cl...Sn = 104.3, 104.8 (1°)] and nearly linear at Sn [Cl(1)—Sn...Cl(1ⁱ) = 172.3 (1), Cl(2)—Sn...Cl(2ⁱⁱ) = 173.1 (1°)]. Overall the geometry at Sn is a distorted AX_4Y_2 octahedron with C—Sn—C, Cl—Sn—Cl, Cl...Sn...Cl, $\langle\text{Cl—Sn—C}\rangle$ and $\langle\text{C—Sn}\cdots\text{Cl}\rangle$ bond angles of 132.1 (7), 97.2 (2), 111.9 (1), 105.6 (4) and 76.8 (4)°, respectively (Fig. 1). The observed Sn—C distances [2.113 (17) and 2.135 (16) Å] are close to standard values [2.135 (35) Å; Britton & Dunitz, 1981] which display no systematic trends with increasing coordination numbers. The two Sn...Cl secondary-bond lengths are significantly different [3.514 (5), 3.544 (5) Å, Δ/σ 4] while the Sn—Cl primary bonds are only marginally different [2.372 (5), 2.388 (5) Å, Δ/σ 2.3]. It is notable that the longer primary bond is *trans* to the shorter secondary bond. Both of the Sn—Cl primary bonds are *ca* 0.09 Å longer than a standard Sn—Cl single-bond distance (2.29 Å; Britton & Dunitz, 1981) while the secondary distances are on average 1.25 Å longer than single-bond distances or, equivalently, are *ca* 0.32 Å shorter than van der Waals limits (Bondi, 1964). The observed *trans* Sn—Cl/Sn...Cl distances and the observed bond angles in Bu_2SnCl_2 are all consistent with the correlations presented by Britton & Dunitz (1981).

The polymeric structure of Bu_2SnCl_2 is very similar to those of Et_2SnCl_2 and Me_2SnCl_2 (Alcock & Sawyer, 1977; Davies, Milledge, Puxley & Smith, 1970). With larger *R* groups, however, the crystal packing is distorted to give one-dimensional polymers with essentially five-coordinate AX_4Y Sn atoms with different axial Cl—Sn...Cl systems in the two forms of $\text{C}_x\text{Y}_2\text{SnCl}_2$ (Ganis *et al.*, 1986; Molloy *et al.*, 1985) and essentially tetrameric units containing both five- and six-coordinate Sn atoms in MePhSnCl_2 and Ph_2SnCl_2 [Amini *et al.*, 1987; see Bokii, Struchkov & Prokofiev (1972) for this interpretation of the Ph_2SnCl_2 structure]. In the latter two compounds some of the longer Sn...Cl secondary bonds are very close to the van der Waals limit. In comparing the effects of the secondary bonding in all of these latter compounds the overall coordination number is probably important and should be

taken into consideration when comparing individual angles.*

Thus in comparing Bu_2SnCl_2 to Et_2SnCl_2 it is notable that the structure of the former has longer Sn...Cl secondary-bond distances, apparently shorter Sn—Cl bonds, smaller CSnC and larger ClSnCl bond angles (Table 3). In the other examples in this table containing 6CN Sn atoms, the parameters for Me_2SnCl_2 are rather inaccurate and need redetermining while in the unsymmetrical MePhSnCl_2 compound the central Sn(1) atom forms unsymmetrical Sn—Cl and Sn...Cl distances which are distinctly correlated. As such the observed CSnC and ClSnCl bond angles for this Sn are not inconsistent with those in Et_2SnCl_2 and Bu_2SnCl_2 . In all the compounds the CSnC angle especially does not show the trends with size of the organo groups that would be expected if this angle was solely the result of steric effects. Furthermore, in solution the ¹³C and ¹¹⁹Sn chemical shifts and the ¹J(¹¹⁹Sn—¹³C) coupling constant are consistent with a four-coordinate species with a CSnC bond angle of only 117° (Holeček *et al.*, 1986), significantly smaller than that observed in the present structure.

In the butyl groups high thermal parameters of some of the peripheral C atoms [notably C(3) and C(4)] have distorted some of the bond lengths and bond angles [notably C(3)—C(4) = 0.98 (8), C(2)—C(3) = 1.77 (6) Å, and C(2)—C(3)—C(4) = 96 (6)°]. Contacts between the butyl groups are ≥ 3.95 Å.

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* Britton & Dunitz (1981) suggest various ways of averaging angles in molecules in which the Sn...Y distances in $\text{SnR}_2\text{X}_2\text{Y}_2$ systems are distinctly unsymmetrical.

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1-Ferrocenyl-9-oxabicyclo[3.3.1]nonan-5-ol*

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Abstract. $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{13}\text{H}_{17}\text{O}_2)]$, $M_r = 326.2$, orthorhombic, $Pbcn$, $a = 28.833$ (4), $b = 12.207$ (3), $c = 8.4933$ (13) Å, $V = 2990$ (2) Å³, $Z = 8$, $D_x = 1.450$ (1) g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 10.1$ cm⁻¹, $F(000) = 1376$, $T = 299$ K, $R = 0.036$ for 1591 data having $F_o^2 > 3\sigma(F_o^2)$ measured by diffractometer. The molecule exists 100% as the lactol with no detectable concentration of the open form as no carbonyl stretch is observed by IR spectroscopy. The Fe atom lies 1.641 (1) and 1.647 (1) Å from the cyclopentadienyl ring planes, and the Fe–centroid vectors form an angle of 177.8°. The cyclopentadienyl rings are twisted 10.4 (3)° from the eclipsed conformation.

Introduction. Since the discovery of ferrocene (Kealy & Pauson, 1951; Miller, Tebboth & Tremaine, 1952), considerable interest has been directed toward preparation of bridged species, with the first being 1,3-(1,1'-ferrocenediyl)-1-propanone (Rinehart & Curby, 1957; Rosenblum, 1953) prepared from an acid-catalyzed cyclization of 3-ferrocenylpropionic acid; the X-ray structure was reported by Jones, Marsh & Richards (1965). The title compound (structure I) is the major product of an attempted synthesis of an ansa-bridged ferrocene derivative (structure II). The MS and elemental analyses were consistent with either structure (Fig. 1). The ¹H 400 MHz NMR spectra indicated structure (I) since the integration of 7:2 accounted for the splitting of the cyclopentadienyl H

atoms as well as an integration of 1 for the hydroxyl H atom. The ¹H NMR spectrum of the alkyl region was second order. The ¹³C and ¹³C DEPT (Derome, 1987) NMR spectra eliminated structure (II) as a possibility; however, the difficulties associated with the observation of quaternary C atoms made assignment to structure (I) inconclusive. The molecule was concluded to exist 100% as the lactol because no carbonyl stretch was observed by IR spectroscopy. Therefore, a single-crystal X-ray structure determination was undertaken to substantiate the ¹H NMR integration results.

Experimental. The *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex of 1,1'-dilithioferrocene was prepared and found to react in high yield with CO₂ and benzophenone (Rausch & Ciappenelli, 1967). The reaction of this material with various diketones is being investigated as a new method to annulate the cyclopentadienyl rings of the ferrocene nucleus.

The cyclic 1,5-diketone, 1,5-cyclooctadione (Kulkarni, Rao & Patil, 1982) reacts with the 1,1'-dilithioferrocene–TMEDA complex in hexane to give the title compound. Crystals, m.p. 414.5–415.5 K

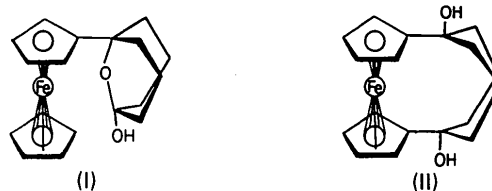


Fig. 1. Possible structures from the reaction of 1,1'-dilithioferrocene with 1,5-cyclooctadione.

* Reactions of 1,1'-Dilithioferrocene with Diketones.

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