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THE CRYSTAL AND MOLECULAR STRUCTURE OF CYCLOPENTADIENYLTIN(II) CHLORIDE. THE BONDING OF THE CYCLOPENTADIENYL GROUP IN TIN(II) COMPOUNDS

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Summary

The crystal and molecular structure of cyclopentadienyltin(II) chloride has been determined from three-dimensional X-ray data. The crystals are orthorhombic, space group $Pc2_1n$. The unit cell, of dimensions $a = 5.711(5)$, $b = 6.225(5)$, $c = 17.24(2)$ Å, contains four molecules. The structure has been refined by full matrix least squares techniques to a final R value of 0.083 for 717 independent reflections. In the crystal unsymmetrical tin—chlorine bridges are present between the units of C_5H_5SnCl.

It is suggested that in cyclopentadienyltin(II) compounds the cyclopentadienyl group occupies more than one coordination site as a result of the donation of π electron density from the cyclopentadienyl ring into an empty acceptor orbital of the tin atom having π symmetry.

Introduction

Although the structural aspects of dicyclopentadienyltin(II) have attracted considerable attention [1-9] no X-ray study has been reported. An electron-diffraction study has shown that dicyclopentadienyltin(II) has an angular sandwich structure in the gas phase [7]. The structure of dicyclopentadienyllead(II) has been determined by X-ray analysis [10]. The dicyclopentadienyllead(II) crystal consists of $Pb—C_5H_5—Pb—C_5H_5$ chains. The coordination of each lead atom is completed by an additional non-bridging C_5H_5 group. The bridging cyclopenta-

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dienyl rings are placed between two metal atoms, at the bisector of, and normal to the metal—metal axis.

It is conceivable that in cyclopentadienyltin(II) chloride bridging cyclopentadienyl groups and/or bridging chlorine atoms are present (cf. the crystal structure of tin(II) chloride [11-13]). For this reason it seemed of interest to obtain more information about the structure of cyclopentadienyltin(II) chloride in the solid.

Experimental

Cyclopentadienyltin(II) chloride was prepared from dicyclopentadienyltin(II) and tin(II) dichloride [14]. Colourless crystals of the air-sensitive compound were obtained by recrystallization from tetrahydrofuran. For the sampling of a single crystal and mounting in a Lindemann capillary, the apparatus described by Van Koten and Boersma [15] was used. The intensity of 717 independent reflections ($\theta < 27°$) was collected with a Nonius CAD 3 diffractometer using Zr-filtered Mo-K_α radiation. The ω-scan technique was used. The data were collected for Lorentz and polarization factors, but no correction for absorption was applied for experimental reasons. The crystal data are as follows: C_5H_5SnCl; Mol. wt. 219.2; orthorhombic; space group $Pc2_1n$ or $Pcmn$; $a = 5.711(5)$, $b = 6.225(5)$, $c = 17.24(2)$ Å; $V = 612.7$ Å^3; $d_{\text{found}} = 2.34$ gcm^{-3}; $d_{\text{calc}} = 2.39$ gcm^{-3}; $Z = 4$; $\mu(\text{Mo-}K_\alpha) = 45.2$ cm^{-1}; general equivalent positions $Pc2_1n$: $\{x, y, z; \frac{1}{2}-x, y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z; -x, \frac{1}{2}+y, -z\}$.

Structure determination and refinement

The observed space group extinctions are consistent with the two space groups $Pc2_1n$ and $Pcmn$. A Patterson synthesis calculated at this point was easily solved for the heavy atom positions. Since the y coordinates of the Sn and Cl atoms thus found are approximately the same, the ambiguity in the choice of the space group was still unresolved. A difference Fourier synthesis calculated on the

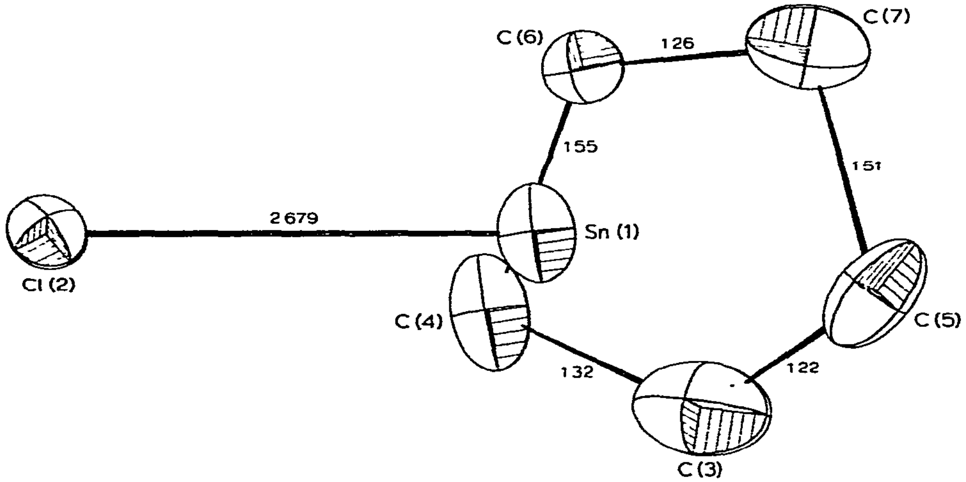

Fig. 1. A thermal-ellipsoid plot with the lengths of the main axes set equal to the root mean square deviations.

TABLE 1

FINAL REFINED ATOMIC PARAMETERS[a] WITH STANDARD DEVIATIONS[b]. THE ANISOTROPIC TEMPERATURE FACTORS ARE OF THE FORM: exp.$[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{23}	β_{13}
Sn(1)	0.0719(2)	0.2500(-)	0.0994(1)	154	440	31	33	—16	—12
Cl(2)	0.0257(8)	0.252(2)	—0.0553(3)	264	247	31	37	—15	—8
C(3)	0.474(6)	0.080(7)	0.154(3)	503	409	94	95	—17	—169
C(4)	0.490(3)	0.174(5)	0.085(1)	80	640	30	132	—48	—26
C(5)	0.413(4)	0.192(5)	0.208(2)	273	524	50	—31	154	—43
C(6)	0.463(3)	0.408(4)	0.115(1)	215	245	35	—27	2	—37
C(7)	0.423(5)	0.427(6)	0.187(2)	321	339	76	—313	—30	—15

[a] The β_{ij} values have been multiplied by 10^4. [b] The standard deviations of the last significant figure are in parentheses.

basis of the heavy atom positions (R = 25%) showed a ring shaped electron density area across the pseudo mirror plane at $y = y(\text{Sn}) \simeq y(\text{Cl})$. Although the position and dimensions of this electron density pattern were as expected for a cyclopentadienyl ring, it showed six maxima rather than five. At first several disordered models in the space group *Pcmn* were tried, but none of them refined satisfactorily. At this point the symmetry was lowered to $Pc2_1n$ and the model shown in Fig. 1 was tried. The structure refined to a final R value of 0.083 for 717 reflections. Although a final difference Fourier map still showed some unexplained features as high as 1 eA^{-3} indicating probably some disorder of the cyclopentadienyl group, it was considered not worthwhile to include partial disordered models in further refinements. The final refined parameters are shown in Table 1. Scattering factors were taken from the International Tables for X-ray Crystallography [16]. The applied corrections for the anomalous scattering for Sn are $\Delta f' = -0.6$, $\Delta f'' = +1.9$ and for Cl: $\Delta f' = 0.15$ and $\Delta f'' = +0.19$.

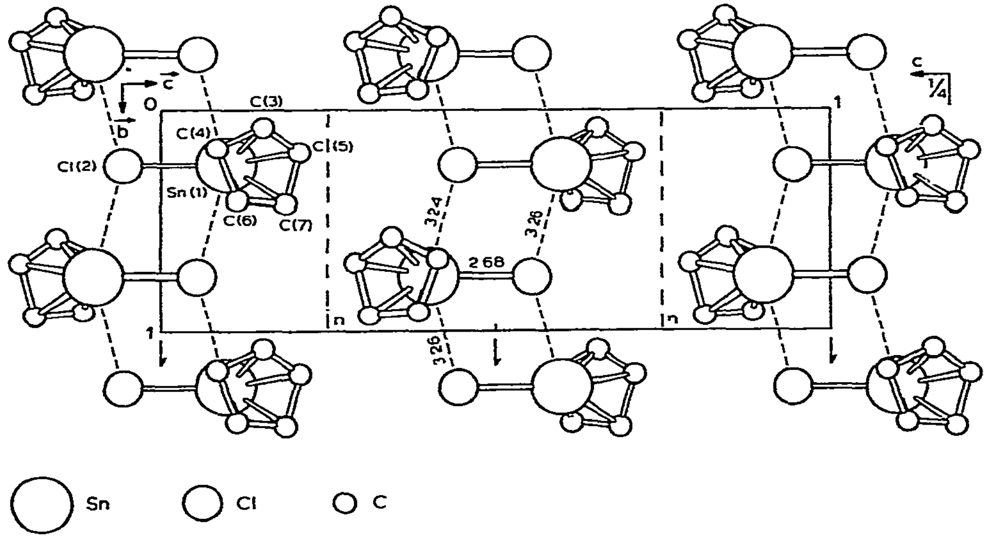

Fig. 2. Projection of the C_5H_5SnCl structure along the a-axis.

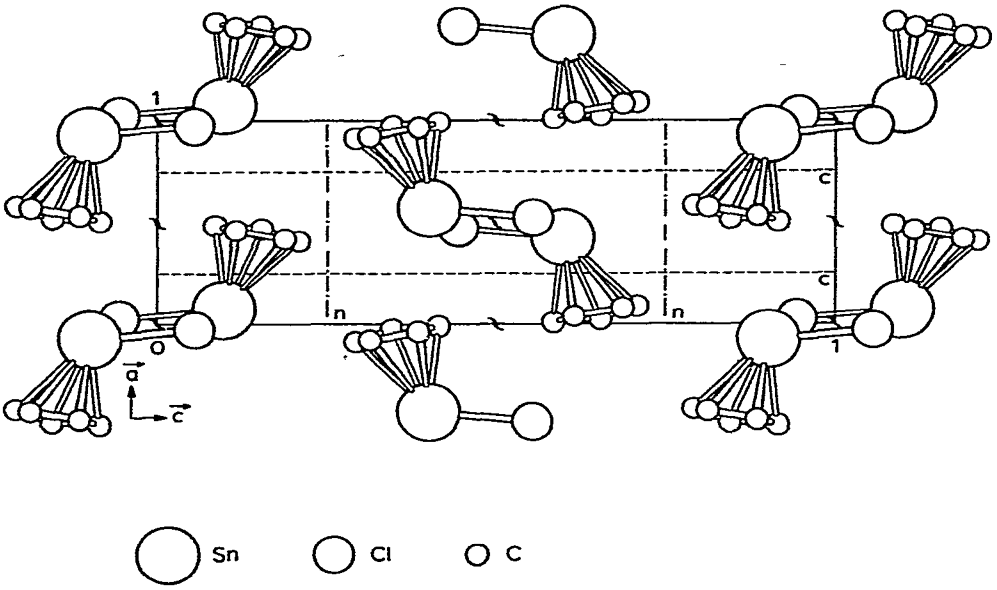

Fig. 3. Projection of the C_5H_5SnCl structure along the *b*-axis.

Results and discussion

The anisotropic temperature movement of the atoms is illustrated in Fig. 1. The temperature factors of the ring carbon atoms are relatively high, indicating probably some rotational disorder. Fig. 2 and Fig. 3 show a projection of the structure along the *a* and the *b* axis, respectively. The bond lengths and some interatomic distances are summarized in Table 2. The bond angles are listed in Table 3. Fig. 4 illustrates the location of the cyclopentadienyl ring with respect to the tin—chlorine axis.

Fig. 2 and Fig. 3 illustrate that on both sides of a Sn—Cl group (and approximately in the same plane) two other Sn—Cl groups are situated in such a manner that a tin atom is surrounded by one near chlorine atom at 2.68 Å and two other chlorine atoms at 3.24 and 3.26 Å. Although the distances of 3.24 and 3.26 Å are very long compared to the value of 2.31 Å for the Sn—Cl bond length in gaseous $SnCl_4$ [17] or the value of 2.42 Å for the Sn—Cl bond length in gaseous $SnCl_2$ [18] this does not rule out a tin—chlorine interaction which will have consequences for the packing of the C_5H_5SnCl units in the crystal (cf. the discussion concerning the unsymmetrical tin—chlorine bridges in the crystal structure of Me_2SnCl_2 [19].

In solid tin(II) chloride —Sn—Cl—Sn—Cl-chains are present, with Sn—Cl distances of 2.78 Å. An additional non-bridging chlorine atom is bonded to each tin atom at a distance of 2.67 Å. The tin atom and the three chlorine ligands form a trigonal pyramid with the tin atom at the apex. Five other chlorine atoms are positioned around the tin atom at distances of 3.06, 3.06, 3.22, 3.30, 3.86 and 3.86 Å [11-13].

Dicyclopentadienyltin(II) in the gas phase has an angular sandwich structure with Sn—C(ring) distances of 2.71 Å [7]. In the cyclopentadienyltin(IV)

TABLE 2

SOME RELEVANT INTERATOMIC DISTANCES INCLUDING BOND LENGTHS (Å) WITH STANDARD DEVIATIONS

Atom 1	Atom 2	Symmetry transformation of atom 2	Distance
Sn(1)	Cl(2)		2.679(5)
Sn(1)	C(3)		2.69(4)
Sn(1)	C(4)		2.45(2)
Sn(1)	C(5)		2.73(3)
Sn(1)	C(6)		2.46(2)
Sn(1)	C(7)		2.74(3)
C(3)	C(4)		1.32(5)
C(4)	C(6)		1.55(4)
C(5)	C(7)		1.51(5)
C(6)	C(7)		1.26(5)
C(3)	C(5)		1.22(5)
Sn(1)	Cl(2)	$-x, -\frac{1}{2}+y, -z$	3.242(5)
Sn(1)	Cl(2)	$-x, \frac{1}{2}+y, -z$	3.262(5)
Sn(1)	C(3)	$-1+x, y, z$	3.70(4)
Sn(1)	C(4)	$-1+x, y, z$	3.36(2)
Sn(1)	C(5)	$-1+x, y, z$	4.22(3)
Sn(1)	C(6)	$-1+x, y, z$	3.63(2)
Sn(1)	C(7)	$-1+x, y, z$	4.15(3)

compound $(\sigma\text{-}C_5H_5)_2Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2$ which contains σ-bonded cyclopentadienyl groups, a Sn—C bond length of 2.18 Å has been found [20]. The observed Sn—C bond lengths which range from 2.45 to 2.75 Å indicate that the cyclopentadienyl ring in solid cyclopentadienyltin(II) chloride is similarly bonded as in dicyclopentadienyltin(II) (see discussion below). The observation that the five ring carbons are not equidistant to the metal atom (cf. Fig. 4) has also been made for $Me_2(C_5H_5)Al$ in the gas phase [21].

The projection of the structure along the *b* axis (Fig. 3) suggests that in cyclopentadienyltin(II) chloride $Sn—C_5H_5—Sn—C_5H_5$ chains are present. However, as compared with the distances from the ring carbon atoms to the nearest tin atom (2.45-2.74 Å) the distances to the next nearest tin atom are much larger (3.36-4.22 Å). Therefore, it is concluded that the cyclopentadienyl rings are terminal rather than bridging.

TABLE 3

BOND ANGLES (°) WITH STANDARD DEVIATIONS

C(4)—C(3)—C(5)	117(4)
C(3)—C(4)—C(6)	96(2)
C(3)—C(5)—C(7)	111(3)
C(4)—C(6)—C(7)	116(2)
C(5)—C(7)—C(6)	99(3)
Cl(2)—Sn(1)—C(3)	115.5(8)
Cl(2)—Sn(1)—C(4)	89.9(5)
Cl(2)—Sn(1)—C(5)	139.0(4)
Cl(2)—Sn(1)—C(6)	101.5(6)
Cl(2)—Sn(1)—C(7)	128.3(6)

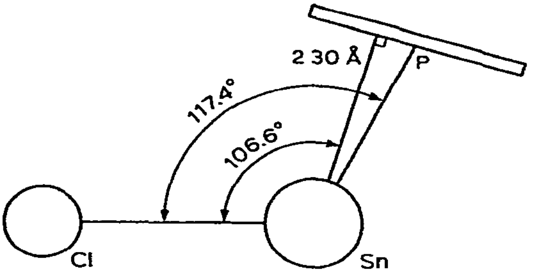

Fig. 4. The position of the cyclopentadienyl ring relative to the tin and chlorine atom. P denotes the centre of the ring.

The bonding in cyclopentadienyltin(II) compounds

Earlier workers have proposed that the hybridization of the tin atom in dicyclopentadienyltin(II) is sp^2 and that the cyclopentadienyl rings are centrally σ-bonded (pseudo π) to the central metal atom [4,5,9]. In this picture the two cyclopentadienyl rings and the lone pair are situated around the tin atom with angles of about 120°. Perpendicular to the sp^2 orbitals an empty p orbital is present.

The donor character expected for dicyclopentadienyltin(II) has been confirmed by the isolation of a complex with the Lewis acid boron trifluoride [22]. Moreover a complex of bis(methylcyclopentadienyl)tin(II) with aluminium trichloride has been reported [23]. However, attempts to demonstrate the acceptor character of dicyclopentadienyltin(II) by the formation of complexes with appropriate nitrogen ligands remained in vain [24].

In solid cyclopentadienyltin(II) chloride a tin atom is surrounded by only one near chlorine atom (at 2.68 Å), by two next nearest-neighbour chlorine atoms (at 3.24 and 3.26 Å) and by one near cyclopentadienyl ring. This contrasts with the coordination of the tin atom in tin(II) chloride where a tin atom has three nearest-neighbour chlorine atoms (at 2.66, 2.78 and 2.78 Å) and five next nearest-neighbour chlorine atoms at distances ranging from 3.06 to 3.86 Å (the sum of the Van der Waals radii of tin and of chlorine is 4.0 Å [25]). Moreover, tin(II) chloride readily forms 1/1 and 1/2 complexes with a large variety of donor molecules [26].

In view of the differences in coordination environment of tin(II) chloride and cyclopentadienyltin(II) chloride and the observation that in contrast with tin(II) chloride, dicyclopentadienyltin(II) does not show acceptor character, we suggest that the "empty" p orbital of the tin atom in dicyclopentadienyltin(II) and in cyclopentadienyltin(II) chloride is actually occupied as a result of the donation of π electron density from the cyclopentadienyl ring into this orbital. This implies that the cyclopentadienyl group in cyclopentadienyltin(II) compounds can occupy two coordination sites rather than one. A similar proposal has recently been put forward for the cyclopentadienyl groups in dicyclopentadienylgermanium(II) [27] and in dimethylcyclopentadienylaluminium [21].

It is well known that diorganotin(II) species R_2Sn: (R = an unsubstituted alkyl or aryl group) cannot be isolated because they readily react to give polymeric or oligomeric tin(IV) compounds containing tin—tin bonds [28]. Contrary to the report that dicyclopentadienyltin(II) readily undergoes polymerization

[22]*, we have observed that this compound does not polymerize on storage in a nitrogen atmosphere at room temperature during more than two years. This low tendency towards polymerization is in agreement with the proposed non-availability of the "empty" *p* orbital at the tin atom.

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[*] Prof. J.J. Zuckerman recently informed us that the polymerization of dicyclopentadienyltin(II) requires the presence of base [29].