749. *The Structures of Dicyclopentadienyl-tin and -lead.*

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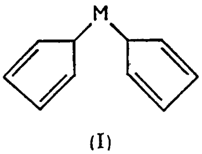
Infrared, nuclear magnetic resonance, ultraviolet, and dipole-moment measurements have been made on the dicyclopentadienyl-tin and -lead compounds and their methyl-substituted derivatives. The structures of these compounds are discussed and evidence for an angular sandwich structure is presented.

The cyclopentadienyl-tin(II)[1] and -lead(II)[2] compounds $(C_5H_5)_2Sn$ and $(C_5H_5)_2Pb$ were prepared by Fischer and his co-workers, who suggested for them the σ-bonded structure (I); this suggestion was supported by the dipole moments of the compounds,[3] the values being $\mu[Sn(C_5H_5)_2] = 1{\cdot}02 \pm 0{\cdot}06$ D and $\mu[Pb(C_5H_5)_2] = 1{\cdot}63 \pm 0{\cdot}06$ D, it being taken that $P_A = 0{\cdot}1P_E$.

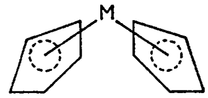
That the σ-bonded structure was unlikely was shown by the measurements of their infrared spectra in carbon tetrachloride solution by Lindstrom and Barusch.[4] The remarkable similarity of these spectra to that of ferrocene led these workers to conclude that the tin and lead compounds had similar sandwich-bonded or π-cyclopentadienyl rings bound to the metal atom. Since such a conclusion could be reconciled with the dipole-moment evidence, if correct, only by assuming that the two metal–ring bonds were at an angle (II), it seemed desirable to confirm the published data and obtain additional evidence.

Infrared Spectra.—The spectra have been measured, in a vacuum, in solution in carbon disulphide and tetrachloroethylene; measurements were also initially made in carbon tetrachloride but, as a slow chemical reaction sets in, this solvent was less suitable. The results are given in Table 1, together with those for ferrocene[5] for comparison. The recent measurements of the infrared spectra of these compounds, reported by Fritz,[6] are so much at variance with the solution data given here and previously[4] that they can only be considered as unreliable. The discrepancy is probably due to the difficulty of preparing halide discs of these air-sensitive substances without extensive decomposition.

The close similarity of the infrared spectra of the tin and lead compounds to each other and to ferrocene is thus confirmed, showing that the three compounds have a basically similar (sandwich) structure. However, there are two possibilities for the tin and the lead cyclopentadienyls: an axial sandwich structure of the ferrocene type (III) and an angular sandwich structure (II). It is theoretically possible to distinguish between the two possible structures from the infrared studies. The axial sandwich belongs to the D_{5d} group whereas the angular one has a much lower symmetry, *viz.*, C_{2v}, the rings being assumed to be freely rotating. From the similarity of the infrared spectra, it might appear that the tin and lead compounds have a ferrocene-like structure. However, the local symmetry of each delocalised ring (D_{5h}) is the same for both types of structure and hence the ring vibrations, *e.g.*, the C–H stretch or bend, C–C stretch, etc., would be very similar.



(I)



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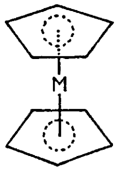

(III)

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[1] Fischer and Grubert, *Z. Naturforsch.*, 1956, **11***b*, 423.
[2] Fischer and Grubert, *Z. anorg. Chem.*, 1956, **286**, 237.
[3] Weiss, *ibid.*, 1956, **287**, 236.
[4] Lindstrom and Barusch, 131st Amer. Chem. Soc. Meeting, Miami, 1957, Abstract 77.
[5] Lippincott and Nelson, *Spectrochim. Acta*, 1958, **10**, 307.
[6] Fritz, *Chem. Ber.*, 1959, **90**, 780.

The presence of the central metal atom can affect the infrared spectrum in the following ways:

(1) For D_{5d} symmetry, which is higher than D_{5h}, the selection rules will be more stringent and fewer vibrations will be infrared-active. For C_{2v} symmetry, on the other hand, the symmetry becomes lower and hence more vibrations will appear in the infrared region. A comparison of the infrared spectra of the tin and the lead compound on the one hand and ferrocene on the other shows several weak bands in the former that are not observed in the latter, consistently with the lower symmetry.

TABLE 1. *Infrared spectra of cyclopentadienyl-tin and -lead, with sodium chloride optics unless otherwise stated.*

$Sn(C_5H_5)_2$		$Pb(C_5H_5)_2$		$Fe(C_5H_5)_2$ [a]
C_2Cl_4	CS_2	C_2Cl_4	CS_2	
3100 [b] s(sh.)	3100 [b] s(sh.)	3090 [b] s(sh.)	3090 [b] s(sh.)	3085 s
3094 [b] s	3094 [b] s	3082 [b] s	3082 [b] s	3075 m(sh.)
2919 [b] w	2918 [b] w	2917 [b] w	2917 [b] w	
2695 w	2695 [b] w	2680 w		
2280 w		2278 w		
2210 w		2200 w		
2085 w		2080 w		
			1745 m	1758 m
1750 m	1750 m	1732 m	1720 m	1720 m
1632 m				1684 m
				1650 m
		1622 m		1620 m
1532 m		1515 m		
1482 w		1482 w		
1426 s		1427 s		1411 s
	1360 m		1351 m	
	1340 m			
1260 w	1260 w	1255 w	1260 w	
1228 w	1228 w	1228 w	1228 w	
	1193 vw		1190 vw	1188 w
	1156 w		1156 w	
	1112 s		1113 s	1108 s
			1082 vw	
1055 w	1055 w	1055 w	1052 w	1051 w
	1002 s		1005 s	1002 s
				834 w
	805 w		805 w	
	780 m		780 w	
	748 vs		750 vs	811 s
666 [c] w	666 w	666 [c] w	666 w	782 w
				492 s
				478 s

[a] See Ref. 5. [b] Measurements using calcium fluoride prism and 1·0 mm. silica cell. [c] No new bands found from 700 to 400 cm.$^{-1}$ in tetrachloroethylene solution with potassium bromide optics.

(2) More striking differences can be expected for the metal–ring stretches. Lippincott and Nelson [5] considered ferrocene as a linear XY_2 molecule so that only the asymmetric stretch is infrared-active; they assigned the band at 478 cm.$^{-1}$ to this vibration. Since an angular sandwich may, similarly, be considered as an angular triatomic molecule, XY_2, both the symmetric and the asymmetric vibrations should be infrared-active. Since the tin and the lead compound are thermally less stable than ferrocene, it seems likely that the metal–ring stretches would here lie below that in ferrocene (478 cm.$^{-1}$). No new bands in the region 700—400 cm.$^{-1}$ were observed and the metal–ring stretches probably lie at still lower frequencies. The very strong band in the spectra of both the tin and the lead compound at *ca.* 750 cm.$^{-1}$ is too high to be a metal–ring stretch. We assign it as a C–H bend ($\perp$) which would correspond to the similar 811 cm.$^{-1}$ and 773 cm.$^{-1}$ bands in ferrocene and nickelocene, respectively.[5]

The infrared spectra of the di(methylcyclopentadienyl)-tin and -lead compounds were also measured from 4000—400 cm.$^{-1}$. They are, in general, similar to those of the dicyclopentadienyl-tin and -lead except for the presence of vibrations due to the methyl groups.

Nuclear Magnetic Resonance Studies.—The high-resolution nuclear magnetic resonance spectra of $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ show only one main proton line at 175 c./sec. and 193 c./sec., respectively, relative to cyclohexane on the low-field side. A sandwich structure, with rings freely rotating as in ferrocene,[7] gives only one line. The σ-bonded structure (I) would be expected to give a complicated line spectrum owing to the non-equivalence of the five protons on each ring. Such a line pattern is not always found in σ-compounds, however. Thus, π-C_5H_5-(σ-C_5H_5)$Fe(CO)_2$ gives only two lines,[7] one assigned to protons in the π-C_5H_5 ring and the other in the σ-C_5H_5 ring. Similarly, we found that $Hg(C_5H_5)_2$ which, on the basis of its complex infrared structure, is assigned a σ-bonded linear structure,[8] shows, even under very high resolution, only one proton line, as also observed by Strohmeier and Lemmon.[9]

In the tin compound the main proton line has two weaker lines symmetrically disposed about it at a separation of ±15·9 c./sec. Each of these lines is a doublet with a separation of about 0·36 c./sec. These lines presumably arise from those molecules in the mixture which contain the tin isotopes ^{117}Sn (abundance = 7·67%; spin = $\frac{1}{2}$; $\mu = -0{\cdot}9949$ nuclear magnetons) and ^{119}Sn (abundance = 8·68%; spin = $\frac{1}{2}$; $\mu = -1{\cdot}040$ nuclear magnetons). The presence of a nuclear species with spin of $\frac{1}{2}$ would produce a doublet splitting of the resonance of the protons bound to it by electron-pair bonds through indirect spin–spin coupling interaction. The magnitude of this splitting for these two tin isotopes should be in the ratio of their magnetic moments since the chemical bonding is the same; in fact, the observed ratio of the splitting is 0·977 which is, within the limits of error, the same as the ratio $\mu(^{117}Sn)/\mu(^{119}Sn) = 0{\cdot}956$. Similar weak lines could not be detected with $Pb(C_5H_5)_2$ although lead has one isotope, ^{207}Pb, which has abundance = 20·82%, spin = $\frac{1}{2}$, and $\mu = 0{\cdot}5837$ nuclear magnetons. Thus the nuclear magnetic resonance spectra of $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ are consistent with a sandwich structure, but a localised σ-bonded structure cannot be ruled out on this basis alone.

The nuclear magnetic resonance spectra of $Sn(CH_3{\cdot}C_5H_4)_2$ and $Pb(CH_3{\cdot}C_5H_4)_2$ show only two main lines with intensity ratio 5 : 3. If these methyl derivatives were mixtures of several σ-bonded isomers with the methyl group on $C_{(1)}$, $C_{(2)}$, or $C_{(3)}$, a very complicated spectrum would be expected. If only one particular σ-structure was energetically favoured, even then a mutual splitting of the ring and methyl proton lines may be expected. This splitting would be expected for a sandwich structure also. In the latter case, however, the splitting may be extremely small, as in the analogous case of toluene where only two proton lines, one due to the methyl and the other due to the phenyl hydrogen atoms, are observed under normal resolution. Hence the absence of splitting on the two proton lines in these methyl derivatives is consistent with a sandwich structure but does not completely rule out the localised σ-bonded structure.

Dipole Moments.—A decision between the two types of sandwich structure could be made on the basis of dipole-moment measurements. Weiss [3] has determined the moments of cyclopentadienyl-tin and -lead in benzene solution. Since benzene is known, in certain cases, to form polar charge-transfer complexes,[10] and as these compounds are easily decomposed in solution by traces of oxygen, it was thought desirable to determine the dipole moments in a different solvent. In carbon disulphide, we find for $Sn(C_5H_5)_2$, $\mu = 0{\cdot}96 \pm 0{\cdot}06$ D and for $Pb(C_5H_5)_2$, $\mu = 1{\cdot}49 \pm 0{\cdot}06$ D, P_A being taken as 0·1 P_E as was done by Weiss.[3] Our results are thus in fair agreement with those of Weiss. While the present work was in progress, the dipole moments, in cyclohexane, have been reported.[11] The

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[7] Piper and Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **3**, 104.

[8] Piper and Wilkinson, *ibid.*, 1956, **2**, 82.

[9] Strohmeier and Lemmon, *Z. Naturforsch.*, 1959, **14*a***, 109.

[10] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; Orgel, *Quart. Rev.*, 1954, **8**, 422.

[11] Fischer and Schreiner, *Chem. Ber.*, 1959, **90**, 938.

values obtained were $\mu(\mathrm{Sn}) = 0{\cdot}96 \pm 0{\cdot}10$ D and $\mu(\mathrm{Pb}) = 1{\cdot}29 \pm 0{\cdot}04$ D. In view of the different solvent, these values are also consistent with ours.

It is unlikely that the above values of dipole moments can be explained by a large atom polarisation, (P_A), especially in view of the fact that other non-polar cyclopentadienyl compounds have low values of P_A.[11] Even in $Mg(C_5H_5)_2$, where the metal–ring bonds are very polar,[12] P_A is only 31·1% of P_E.[11] Hence we conclude that both these tin and lead compounds have permanent dipole moments.

Visible and Ultraviolet Spectra.—The spectra are given in Table 2. The compounds show, in the ultraviolet region, a band not found in any di-π-cyclopentadienyl metal compound (*e.g.* of V,[13] Cr,[13] Fe,[14] Co,[13] or Ni[13]) or metal cyclopentadienides (Mg,[13] Mn[13]).

These bands show slight " blue shifts " (not very pronounced in the case of the tin compounds) in going from 2,2,4-trimethylpentane to the polar tetrahydrofuran. The spectra were measured up to 220 mμ but in view of the ready hydrolysis of these compounds by even traces of water the results were not considered reliable below 280 mμ and hence are not given.

TABLE 2. *Absorption spectra.*

	$Sn(C_5H_5)_2$		$Sn(CH_3{\cdot}C_5H_4)_2$		$Pb(C_5H_5)_2$	
Solvent	$\lambda_{\max.}$	ε	$\lambda_{\max.}$	ε	$\lambda_{\max.}$	ε
2,2,4-Trimethylpentane	295	4270	305	3600	343	7460
Tetrahydrofuran	293	4300	303	4850	335	7600

Nature of Bonding.—The infrared and the dipole-moment evidence shows clearly that these compounds have angular sandwich structures; nuclear magnetic resonance spectra are consistent with such a formulation. Such a sandwich structure is the first of its kind known and presents an interesting problem as regards bonding. A simple way of considering the bonding is to regard both $Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ as similar to the gaseous stannous and plumbous halides which also have angular structures.[15] The tin and lead atoms may be considered to be in an sp^2 hybrid state. Two hybrid orbitals each containing one electron can then overlap with one orbital of each ring containing one electron to form two single covalent bonds inclined to each other. The third sp^2 hybrid orbital then contains the remaining two electrons as a lone pair. Complete hybridisation may not, of course, occur and the lone pair may have more *s* character and the bonding orbitals more *p* character. The same angular structure would be expected from considerations of electrostatic repulsion between the bonding and the non-bonding electrons.[16] Furthermore, an axial sandwich of the ferrocene type is unlikely since such a structure with linear *sp* hybrid bonds would have the two non-bonding electrons in the degenerate p_x and p_y orbitals. According to Hund's rule, the ground state would be a triplet which is, of course, not observed.

As regards the cyclopentadienyl ring orbitals, the five π electrons can be assigned to the molecular orbitals, a_1, e_1, and e_2, in that order of energy.[17] The electron distribution in its ground state, therefore, is a_1^2, e_1^3, e_2^0. As a_1 is the only orbital with the right symmetry to combine with the hybrid metal orbital, for bonding to occur, one electron from a_1 must be promoted to e_1. This partly filled a_1 ring π-orbital can then overlap the metal orbital to give a σ-bond. Since this ring a_1 orbital is " hollow " (it follows the ring framework and is antisymmetrical to it), its overlap with the metal orbitals is not likely to be efficient, which may explain, in part, the comparative thermal instability of these compounds.

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[12] Wilkinson, Cotton, and Birmingham, *J. Inorg. Nuclear Chem.*, 1956, **2**, 95.
[13] Dave and Wilkinson, unpublished results.
[14] Kaplan, Kester, and Katz, *J. Amer. Chem. Soc.*, 1952, **74**, 5531.
[15] Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.
[16] Gillespie and Nyholm, *Quart. Rev.*, 1958, **11**, 339.
[17] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76**, 3386.

There is also a possibility of secondary π-bonding between the doubly filled four e_1 orbitals of the two rings and the empty p_z and d orbitals of the metal. This will impart some multiple-bond character to the metal–ring bonds but will not affect the free rotation of the two rings as there are two identical e_1 orbitals at right angles to each other on each ring.

EXPERIMENTAL

Preparation of Compounds.—$Sn(C_5H_5)_2$ and $Pb(C_5H_5)_2$ were prepared by the general method of reaction of sodium cyclopentadienide with anhydrous metal salts in tetrahydrofuran.[12,18] High yields were obtained and this procedure was more convenient than those given previously.[1,2] Anhydrous stannous chloride and lead chloride were normally used. Lead acetate, dehydrated by azeotropic distillation with excess of benzene, gave better yields than lead chloride, presumably owing to its higher solubility in the solvent. Lead nitrate, as recommended by Fischer and Grubert,[2] should be avoided as it can lead to violent explosions during sublimation.

The methylcyclopentadienyl compounds were prepared by a similar method from sodium methylcyclopentadienide.[19] The *tin* derivative (Found: Sn, 43·7. $C_{12}H_{14}Sn$ requires Sn 42·88%) is a pale yellow (almost colourless) liquid at room temperature. The *lead* compound (Found: Pb, 57·0. $C_{12}H_{14}Pb$ requires Pb, 56·7%) is a low-melting yellow solid. The lead compound, in the liquid state, readily supercools. The properties of these methyl derivatives are, in general, similar to those of the cyclopentadienyl compounds; they are, however, less stable than the latter to heat and, as expected, to air also.[19]

Solvents.—Contrary to published statements,[1,2] the tin and lead compounds were found to be very sensitive to traces of moisture in the solvents. For all physical measurements except the ultraviolet spectrum, drying over phosphoric oxide or lithium aluminium hydride for *ca.* 3—4 hr. was adequate. For ultraviolet measurements, such a drying of spectroscopically pure solvents always resulted in slightly turbid solutions. It was found necessary to dry (P_2O_5 or $LiAlH_4$) for at least 24 hr. in a vacuum, accompanied by frequent magnetic stirring. During this period the rest of the vacuum line was evacuated and heated. The solvents for all spectral measurements were deoxygenated by cooling in liquid air and evacuating repeatedly. These measurements were repeated after recrystallising the compounds in a vacuum from " AnalaR " light petroleum and resubliming them.

Apparatus and Instruments.—Infrared measurements were made on a Perkin-Elmer Model 21 spectrophotometer with CaF_2, NaCl, and KBr optics. A vacuum cell made of a metal framework to which the appropriate windows were cemented with Araldite and fitted with a copper-to-glass seal was used. The path length was 1·5 mm. The nuclear magnetic resonance spectra were measured at 40 Mc./sec. on a Varian Associates Model 4300B spectrometer with super-stabiliser. The samples, together with a cyclohexane capillary as external reference, were contained in 5-mm. o.d. sample tubes which were sealed in a vacuum. Dipole-moment measurements were made at 25° ± 0·1° on a heterodyne-beat capacitance meter similar to that described by Sutton and Hill [20] with a modified Sayce–Briscoe [21] type cell. All operations were carried out in an atmosphere of dry nitrogen. Visible and ultraviolet spectral measurements were made on a Perkin-Elmer Spectracord 4000 using 1·0 and 10·0 mm. silica cells sealed in a vacuum.

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[18] Wilkinson, *Org. Synth.*, 1956, **36**, 31.
[19] Reynolds and Wilkinson, *J. Inorg. Nuclear Chem.*, 1959, **9**, 86.
[20] Sutton and Hill, *J.*, 1953, 1482.
[21] Sayce and Briscoe, *J.*, 1925, **127**, 315.