

X-Ray Crystal Structures of Bis(cyclopentadienyl)tin and Bis(pentamethylcyclopentadienyl)lead

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Summary The X-ray crystal structures of bis(cyclopentadienyl)tin (**1**) and the new compound bis(pentamethylcyclopentadienyl)lead (**2**) show that (i) both compounds are monomeric in the solid state and (ii) the C₅H₅ and Me₅C₅ rings in compounds (**1**) and (**2**), respectively, are bonded in the pentahapto-manner.

chains with bridging cyclopentadienyl rings.¹ However, we have now found that bis(cyclopentadienyl)tin (**1**) is monomeric in the solid state. Single crystals of compound (**1**)² were grown by sublimation *in vacuo*.

Crystal data: C₁₀H₁₀Sn, *M* = 248.9, orthorhombic, space group *Pbcm*, *a* = 5.835(3), *b* = 25.384(9), *c* = 12.784(5) Å, *U* = 1893.5 Å³, *Z* = 8, *D_c* = 1.75 g cm⁻³, *F*(000) = 960, $\bar{\lambda}$ (Mo-K α) = 0.71069 Å, μ (Mo-K α) = 25.5 cm⁻¹. The

THE solid-state structures of the bis(cyclopentadienyl) compounds of Group 4 representative elements have generally been assumed to comprise polymeric zigzag



structure was solved by direct methods. Full-matrix least-squares refinement using 1193 observed reflections yielded a conventional R value of 0.073.†

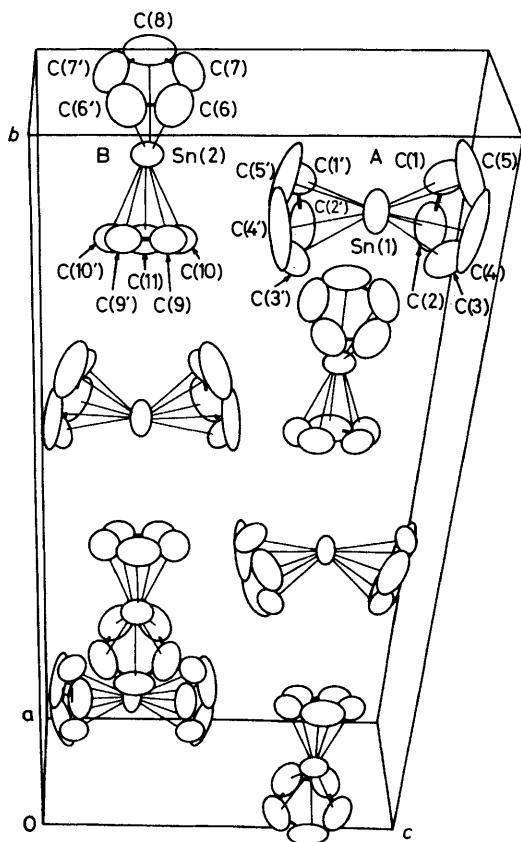


FIGURE 1. Molecular structure and unit cell packing of $(C_5H_5)_2Sn$ (1). Important bond distances (\AA) are Sn(1)–C(1) 2.58(2), Sn(1)–C(2) 2.62(2), Sn(1)–C(3) 2.71(3), Sn(1)–C(4) 2.75(3), and Sn(1)–C(5) 2.68(3) in molecule A, and Sn(2)–C(6) 2.56(2), Sn(2)–C(7) 2.67(2), Sn(2)–C(8) 2.79(3), Sn(2)–C(9) 2.59(2), Sn(2)–C(10) 2.74(2), and Sn(2)–C(11) 2.85(3) in molecule B.

Each unit cell contains four pairs of molecules. The molecules which comprise the pairs each feature a plane of symmetry (Figure 1); in molecule B the plane passes through the Sn atom and bisects both the cyclopentadienyl rings and in molecule A the plane passes through the Sn atom and reflects one cyclopentadienyl ring into the other.

The most interesting aspect of the structure of compound (1) is the fact that it is monomeric in the solid phase. The closest approach of the tin atom of one molecule to a carbon atom of another is 4.02 \AA . The structure of compound (1) is therefore in sharp contrast to that of the lead analogue, $(C_5H_5)_2Pb$, which possesses a zigzag polymeric arrangement with alternating bridging and terminal cyclopentadienyl groups.³

A second noteworthy feature of the structure of compound (1) is that the ring centroid–metal–ring centroid angle V is rather large (148.0° in molecule A and 143.7° in molecule B). In an electron diffraction study of the

vapour-phase structure of compound (1),⁴ this angle was found to be *ca.* 125°; however, as the authors noted, the data were of poor quality on account of extraneous scattering. Interestingly, the average value of V in (1) is *ca.* 1° larger than that in $(Me_5C_5)_2Sn$,⁵ which suggests that this angle may be governed by electronic rather than steric factors.

Because of the polymeric nature of $(C_5H_5)_2Pb$, we synthesized the permethyl analogue $(Me_5C_5)_2Pb$ (2) in the hope that this species would be monomeric in the solid state. Compound (2) was prepared by the slow addition of $PbCl_2$ (0.93 mmol) to a solution of Me_5C_5Li (1.96 mmol) in tetrahydrofuran (45 ml) under a nitrogen atmosphere. Filtration of the reaction mixture afforded a deep red solution, evaporation, under reduced pressure, of which produced compound (2) as a deep red solid, m.p. 100–105 °C. Single crystals of compound (2) were prepared by sublimation *in vacuo*.

Crystal data: $C_{20}H_{30}Pb$, $M = 477.7$, monoclinic, space group $P2_1/n$, $a = 9.771(4)$, $b = 14.751(7)$, $c = 14.517(7)$ \AA , $\beta = 94.75(3)^\circ$, $U = 2085.2$ \AA^3 , $Z = 4$, $D_c = 1.52$ g cm^{-3} , $F(000) = 928$, $\lambda(Mo-K\alpha) = 0.71069$ \AA , $\mu(Mo-K\alpha) = 79.7$ cm^{-1} . The structure was solved by Patterson methods using 1848 observed reflections and was refined to a final R value of 0.031.† Unlike $(C_5H_5)_2Pb$, compound (2) is monomeric in the solid phase. Another interesting feature of the structure of compound (2) (Figure 2) is the fact that V is 151°, and thus larger than that in the analogous tin compound $(Me_5C_5)_2Sn$.⁵ This observation suggests the dominance of the inert pair effect over steric factors.

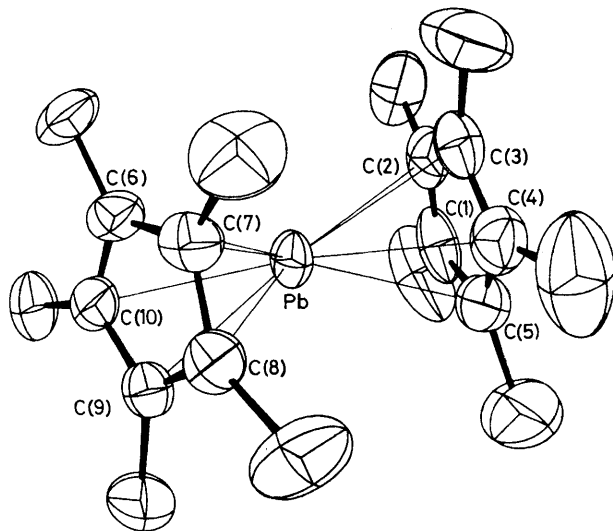


FIGURE 2. Molecular structure of $(Me_5C_5)_2Pb$ (2). Important bond distances (\AA) are Pb–C(1) 2.87(1), Pb–C(2) 2.87(1), Pb–C(3) 2.80(1), Pb–C(4) 2.75(1), Pb–C(5) 2.77(1), Pb–C(6) 2.79(1), Pb–C(7) 2.69(1), Pb–C(8) 2.69(1), Pb–C(9) 2.81(1), and Pb–C(10) 2.90(1).

In compounds (1) and (2) there is a scatter in the ring carbon–element bond distances due to 'ring slippage'. The range for compound (1) is 2.56–2.85 \AA , whilst that for compound (2) is 2.69–2.90 \AA . Values such as these have

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation of this communication.

been observed for substituted cyclopentadienyl groups in transition-metal compounds, where the bonding is clearly pentahapto,⁶ hence compounds (1) and (2) are also best regarded as involving pentahapto-C₅H₅ and -Me₅C₅ rings, respectively.

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¹ See, for example, F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry. A Comprehensive Text,' 4th edn., Wiley-Interscience, New York, 1980, pp. 400—401.

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⁶ For example, in $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_3)_2\text{Zr}(\text{CH}(\text{SiMe}_3)_2)(\text{Cl})]$ the Zr-C(η^5) lengths range from 2.477(8)—2.686(7) Å, M. F. Lappert, P. I. Riley, P. I. W. Yarrow, J. L. Atwood, W. E. Hunter, and M. J. Zaworotko, *J. Chem. Soc., Dalton Trans.*, 1981, 814.