

X-Ray Crystal Structure of an Ionic Trialkyldiaquotin(IV) Cyclopentadiene Derivative, $[\text{Bu}_3\text{Sn}(\text{OH}_2)_2]^+ [\text{C}_5(\text{CO}_2\text{Me})_5]^-$

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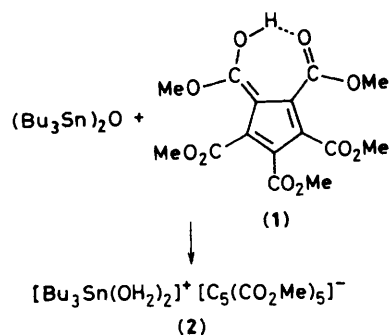
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Penta(methoxycarbonyl)cyclopentadiene reacts with dibutyltin oxide to give the salt $[\text{Bu}_3\text{Sn}(\text{OH}_2)_2]^+ [\text{C}_5(\text{CO}_2\text{Me})_5]^-$; X-ray analysis shows that the cation is trigonal bipyramidal, with apical water molecules.

Trialkyltin compounds may exist as 4-co-ordinate tetrahedral monomers (*e.g.*, R_3SnH) or 5-co-ordinate trigonal bipyramidal monomers or polymers (*e.g.*, $[\text{Me}_3\text{SnClpyridine}]$ or Me_3SnF respectively).¹ The existence of the hydrated trialkyltin cation is recognised in aqueous solution,² and the crystalline salt $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]^+ [\text{BPh}_4]^-$ has been isolated,³ but it has never been characterised crystallographically. We report here the identification of this unit, in a novel combination with the penta(methoxycarbonyl)cyclopentadienyl anion.

The salt (2) separated in about 75% yield when a solution of dibutyltin oxide and penta(methoxycarbonyl)cyclopentadiene (1) in benzene was left overnight; presumably adventitious water is derived from the solvent.



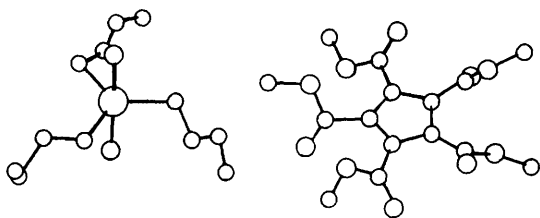


Figure 1. Molecular structure of $[\text{Bu}_3\text{Sn}(\text{OH}_2)_2]^+[\text{C}_5(\text{CO}_2\text{Me})_5]^-$ (2).

The structure of (2)[†] is shown in Figure 1. The symmetry of the cation is close to D_{3h} , with bond lengths Sn–C 2.190(14), 2.155(12), and 2.189(11) Å, Sn–O 2.295(4) and 2.326(5) Å, and an angle OSnO of 178.4(2)°.

In the cyclopentadienyl anion, the five carbon atoms of the ring and the five attached carbonyl carbon atoms are essentially coplanar, and the lengths of the carbon–carbon bonds within the ring are equal within experimental error [1.402(9)—1.420(8) Å]. The methoxycarbonyl groups are all twisted out of the plane of the ring by between 29.2 and 53.2°.

All the cyclopentadienyltin(IV) compounds which have been investigated previously have been covalently η^1 -bonded.⁴ The

[†] Crystal data: $\text{C}_{12}\text{H}_{31}\text{O}_2\text{Sn} \cdot \text{C}_5\text{H}_5\text{O}_2$, $M = 681$, monoclinic, space group $P2_1/n$, $a = 12.118(5)$, $b = 19.203(3)$, $c = 14.526(6)$ Å, $\beta = 96.73(3)^\circ$, $Z = 4$, $D_c = 1.348 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 8.1 \text{ cm}^{-1}$, 2249 observed out of 4454 measured reflections [$I > 1.50\sigma(I)$], data measured to $\sin\theta/\lambda = 0.527 \text{ \AA}^{-1}$, $R = 0.059$ (anisotropic thermal parameters for all non-hydrogen atoms, except the butyl carbon atoms). 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 for this communication.

Li, K, Tl,⁵ Ba,⁶ and Cr^{III}⁷ derivatives of $\text{HC}_5(\text{CO}_2\text{Me})_5$ have a fulvenoid structure similar to that of the protic parent (1).⁵ Both rings have been shown to be η^5 -bonded in the ruthenium derivative $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\{\eta^5\text{-C}_5(\text{CO}_2\text{Me})_5\}]$,⁸ but the anion in (2) has been shown to be present also in the compounds $[\text{H}_2\text{Ru}(\text{PPh}_3)_2\text{C}(\eta^5\text{-C}_5\text{H}_5)]^+[\text{C}_5(\text{CO}_2\text{Me})_5]^-$,⁹ $[\text{Os}(\text{NCMe})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]^+[\text{C}_5(\text{CO}_2\text{Me})_5]^-$,¹⁰ and $[\text{Rh}\{\eta^5\text{-C}_5\text{H}_2(\text{CO}_2\text{Me})_3\}_2]^+[\text{C}_5(\text{CO}_2\text{Me})_5]^-$.¹¹

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