Metal Ion–Aromatic Complexes. XXII. The Preparation, Structure, and Stereochemistry of Tin(II) in π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$

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Abstract: The compound π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$ has been prepared and its crystal structure has been solved. The geometry of the Sn(II) can be described in terms of a pentagonal bipyramid with five equatorial chlorine atoms, one axial chlorine, and the other axial position occupied by the center of a benzene ring. The remaining benzene is far removed from the metal and appears to be only a molecule of solvation. The overall structure may be described as a chain structure in which AlCl$_4^-$ tetrahedra are bridged together by Sn(II). The other AlCl$_4^-$ functions as a chelating ligand to form an axial and an equatorial Sn–Cl bond. The Sn–Cl distances vary from 2.766 (2) to 3.280 (2) Å. The average Sn–C (bound) distance is 3.06 Å and the Sn–center of ring distance is 2.74 (1) Å. A qualitative molecular orbital model is presented and adequately accounts for many of the Sn(II) coordination features. The Mössbauer spectrum consists of a single line with an isomer shift of 3.93 ± 0.1 mm/sec relative to BaSnO$_3$. The crystal data are: monoclinic, $P2_1/n$; $a = 11.282$ (3), $b = 17.317$ (8), $c = 12.646$ (6) Å; $\beta = 110.08$ (1)°; λ 0.71068 Å; $\rho_o = 1.7$–2.0, $\rho_c = 1.77$ g cm^{-3}; $Z = 4$; π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$; $\mu = 21.1$ cm^{-1}. The structure was determined from 3280 counter measured intensity data at room temperature and refined by full-matrix least-squares including anomalous dispersion corrections for Sn and Cl. All temperature factors were refined anisotropically. The refinement converged to a final R of 0.035.

The interaction of metal ions as acceptors with aromatic molecules as donors has been the object of interest for a number of years.[1] These donor–acceptor complexes are interesting, not only because of the nature of the chemical binding between donor and acceptor but also due to the fact that appropriate members of this series have solution properties which indicate that they can act as carriers for aromatics,[2,3] low molecular weight olefins,[2a] and small molecules such as CO, NO, CS$_2$, and SO$_2$.[2b]

As part of a systematic examination of complexes between the post-transition-metal ions and aromatics, we have found compounds between Sn(II) and aromatic moieties to be of two general types: (1) π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$,[4] the subject of the present contribution, and (2) (π-ArSn-Cl)$_2$(AlCl$_4$)$_2$,[5] a dimer containing halogen-bridged Sn(II). A preliminary communication on π-C$_6$H$_6$Sn-(AlCl$_4$)$_2$·C$_6$H$_5$[4b] has appeared and established the stereochemistry about the Sn(II) entity as pentagonal bipyramidal with an axially symmetric interaction between Sn(II) and benzene. We have since completely remeasured the diffraction data and refined the structure to a superior degree. We report here the details of the preparation, structure analysis, Mössbauer spectra, and our interpretation of the bonding in this compound as well as the bonding in the geometrically related C$_6$H$_6$·U(AlCl$_4$)$_3$[6] and the relationship of compounds of type 1 to compounds of type 2.

Experimental Section

Anhydrous stannous chloride (4.0 g, 21 mmol) and aluminum chloride (8.0 g, 60 mmol) were placed in one arm of an H-tube[7] under a nitrogen atmosphere. Benzene (50 ml, distilled from CaH$_2$ under a nitrogen atmosphere) was placed in the other arm. After degassing, it was distilled onto the SnCl$_2$–AlCl$_3$ mixture by immersing one arm of the H-tube in a liquid nitrogen trap. The reaction mixture was allowed to come to room temperature and then heated for 2.5 hr in an oil bath at 80°C. While the reaction mixture was still warm it was filtered in vacuo and the excess solvent removed by immersing one arm of the H-tube in a liquid nitrogen trap until crystals formed.

Colorless diffraction-quality crystals were obtained by repeated recrystallization from benzene. The crystals were coated with petroleum jelly and sealed in Lindemann capillaries to prevent decomposition by water vapor and loss of aromatic. Preliminary Weissenberg and precession photographic data $hk0$, $hk1$ ... $hk7$,

$h0l$, $0kl$ zones showed the crystals to be monoclinic with the systematic absences $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, establishing the space group as $P2_1/n$.[8]

A single crystal 0.39 × 0.47 × 0.73 mm was mounted with the long direction approximately parallel to the ϕ axis on a FACS-1 Picker diffractometer equipped with a graphite monochrometer and aligned by variations of well-known techniques.[9] A least-squares fit[9c] of the χ, ϕ, and 2θ angles of 16 reflections accurately centered on the diffractometer was used to determine the lattice constants at 23–25°C (λ 0.71068 Å for Mo Kα): $a = 11.282$ (3), $b = 17.317$ (8), $c = 12.646$ (6) Å; $\beta = 110.08$ (1)°. With $Z = 4$ the calculated density is 1.77 g cm^{-3} and the observed density is between 1.7 and 2.0 g cm^{-3}. A more accurate value was unattainable because the crystals decompose very rapidly in halocarbon solution. The linear absorption coefficient μ was calculated to be 21.1 cm^{-1} with Mo Kα radiation. With this μ and the above crystal dimensions the variation in transmission coefficient was found to be 0.421–0.479.[10a] A total of 6900 independent hkl reflections were measured by θ–2θ scan techniques to $2\theta_{max} = 65°$ with monochromated Mo Kα radiation at room temperature for 47.70 sec at 0.034°/sec and background counts were made for 40 sec total (B_1 and B_2). Intensities were measured for only the independent octants hkl and $-hkl$. Reflections were considered absent if the integrated intensity was less than $2[(1.193)^2(B_1 + B_2)]^{1/2}$. By this criteria 3280 reflections were retained as being nonzero. A standard general reflection was measured every tenth reflection to ensure stability of operation and to monitor any crystal decomposition.[10b] Some decomposition of crystal was noted during data collection as indicated by loss in intensity of the standard reflection. This loss in intensity, however, was only 7% of total intensity, while the variation from one measurement of the standard reflection to the next was well within counting statistics, σI(net) = [I(scan) + $(1.193)^2(B_1 + B_2)]^{1/2}$. The intensities of several symmetry-related reflections were recorded and the variation of intensity from one reflection to its symmetry-related partner was less than 4% of the total integrated intensity. The takeoff angle, source-to-crystal distance, and crystal-to-counter distance were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperture at the counter was 6 × 8 mm. The half-width at half peak height for an average reflection was 0.21° at a takeoff angle of 3.7°, indicating a mosaic spread such that all the reflection was counted during the 1.6° scan. The 0.21° is not an absolute value of the mosaic spread but is dependent upon other instrumental factors as well. The counting rate never exceeded 5000 counts/sec, and thus no attenuators were used. The pulse height analyzer was set such that 90% of the scattered radiation was counted. Lorentz–polarization corrections were made to reduce the intensities to relative structure factors. A

Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	Atom	x	y	z
Sn	0.2478 (1)	0.1588 (0)	−0.1170 (1)	C(1)	0.1865 (14)	0.0114 (6)	−0.0875 (18)
Cl(1)	0.0723 (2)	0.2954 (1)	−0.1516 (2)	C(2)	0.2022 (11)	0.0211 (8)	−0.1079 (14)
Cl(2)	0.1151 (2)	0.1881 (1)	−0.3548 (2)	C(3)	0.1186 (14)	0.0760 (8)	0.0285 (10)
Cl(3)	0.0160 (2)	0.3821 (1)	−0.4181 (2)	C(4)	0.0227 (11)	0.0972 (6)	−0.0619 (13)
Cl(4)	−0.1903 (2)	0.2503 (1)	−0.3891 (2)	C(5)	0.0057 (10)	0.0675 (8)	−0.1647 (11)
Cl(5)	0.4610 (3)	0.2317 (2)	−0.3963 (2)	C(6)	0.0848 (16)	0.0136 (9)	−0.1828 (12)
Cl(6)	0.4036 (2)	0.0862 (1)	−0.2274 (2)	C(7)	0.3478 (12)	0.0137 (11)	−0.6312 (13)
Cl(7)	0.4048 (2)	0.2717 (1)	−0.1501 (2)	C(8)	0.3178 (16)	−0.0461 (9)	−0.5776 (14)
Cl(8)	0.6896 (2)	0.1845 (2)	−0.1363 (2)	C(9)	0.2323 (15)	−0.0407 (8)	−0.5259 (12)
Al(1)	0.0028 (2)	0.2811 (1)	−0.3292 (2)	C(10)	0.1701 (13)	0.0280 (9)	−0.5281 (11)
Al(2)	0.4993 (2)	0.1937 (2)	−0.2332 (2)	C(11)	0.1954 (12)	0.0918 (8)	−0.5822 (11)
				C(12)	0.2830 (14)	0.0854 (8)	−0.6383 (11)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	70 (1)	38 (0)	73 (0)	−4 (0)	21 (0)	2 (0)
Cl(1)	116 (2)	59 (1)	61 (2)	20 (1)	8 (2)	−12 (1)
Cl(2)	113 (2)	56 (1)	63 (2)	25 (1)	13 (2)	−8 (1)
Cl(3)	112 (3)	47 (1)	106 (2)	−11 (1)	30 (2)	7 (1)
Cl(4)	77 (2)	53 (1)	82 (2)	8 (1)	14 (1)	6 (1)
Cl(5)	163 (3)	83 (2)	91 (2)	1 (2)	52 (2)	22 (2)
Cl(6)	115 (2)	39 (1)	110 (2)	−4 (1)	51 (2)	−9 (1)
Cl(7)	100 (2)	36 (1)	99 (2)	−4 (1)	43 (2)	−4 (1)
Cl(8)	78 (2)	69 (1)	142 (3)	6 (1)	18 (2)	7 (2)
Al(1)	75 (2)	39 (1)	57 (2)	4 (1)	12 (2)	−2 (1)
Al(2)	77 (2)	42 (1)	77 (2)	2 (1)	31 (2)	5 (1)
C(1)	207 (16)	36 (5)	339 (21)	−2 (6)	194 (17)	15 (8)
C(2)	113 (13)	72 (6)	219 (15)	−31 (7)	1 (11)	68 (8)
C(3)	199 (17)	78 (7)	126 (13)	−75 (9)	73 (13)	−14 (7)
C(4)	125 (13)	43 (5)	234 (16)	−16 (7)	107 (12)	8 (8)
C(5)	113 (11)	78 (7)	162 (14)	−45 (7)	7 (10)	29 (8)
C(6)	255 (21)	74 (6)	169 (14)	−80 (10)	102 (15)	−45 (8)
C(7)	159 (16)	93 (9)	178 (16)	1 (10)	64 (13)	−35 (9)
C(8)	202 (19)	67 (7)	188 (17)	25 (10)	34 (14)	1 (9)
C(9)	222 (20)	60 (7)	150 (14)	2 (10)	16 (13)	17 (8)
C(10)	191 (17)	72 (7)	155 (13)	−32 (9)	55 (12)	−35 (8)
C(11)	167 (15)	61 (6)	154 (13)	0 (8)	47 (11)	−11 (7)
C(12)	217 (19)	62 (7)	153 (14)	−24 (14)	42 (13)	−11 (7)

[a] Anisotropic temperature factors of the form $[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$.
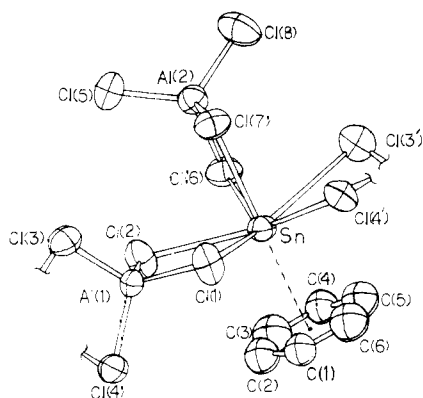

Figure 1. An ORTEP[19] plot with ~50% probability ellipsoids showing the local environment about the Sn(II) in π-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$. The equatorial plane of the pentagonal bipyramid is made up of Cl(1), Cl(2), Cl(6), Cl(3′), and Cl(4′). The axial coordination sites are Cl(7) and the center of the benzene ring. The primed atoms are related crystallographically to the unprimed and constitute the repeat to form the Sn(AlCl_4)_2 chain.

monochrometer correction of 12.50° was applied.

Solution of Structure. A three-dimensional Patterson function[11] was computed and gave the positions of tin and the chlorine atoms. The remaining nonhydrogen atoms were located by standard heavy atom techniques. Three cycles of full-matrix isotropic least squares[12a] gave a conventional R of 0.101.[12b] A further five cycles of full-matrix anisotropic least-squares for all nonhydrogen atoms yielded 0.035 and 0.049 for R and the weighted R_w.[13] The final parameter shifts were 0.1σ or less. We minimized the function $\Sigma w(|F_o| - |F_c|)^2$ and the observations were weighted on counting statistics and a 4% intensity factor.[14] The scattering fac-

tors Sn^{2+}, neutral chlorine, aluminum, and carbon were from Cromer and Waber.[15] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c; the values for $\Delta f'$ and $\Delta f''$ for tin and chlorine were those given by Cromer.[16]

The final tabulation of observed and calculated structure factors is filed elsewhere.[17] Unobserved data were not used in the refinement but are listed with the calculated structure factors. Final atomic coordinate and temperature parameters are in Table I. Interatomic distances, angles, and effors are shown in Table II.[18] The least-squares planes and root-mean-square components of thermal displacements are in Tables III and IV, respectively.

Results

The structure of π-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$ may be described as a Sn(II) moiety bonded to two chlorine atoms from each of three different tetrachloroaluminate ions (Figures 1 and 2).[19] This corresponds to edge sharing of tetrahedral $[AlCl_4^-]$ to form a linear chain structure propagating in approximately the [101] direction (Figure 2). Two chlorine atoms on one tetrachloroaluminate (Cl(8) and Cl(5)) are not bound to any tin atom, whereas all chlorine atoms of the other tetrachloroaluminates are involved in Sn–Cl interactions (Figure 2). The Sn(II) coordination polyhedron is completed by a symmetrical axial interaction to the benzene ring bound to the $Sn^{II}(AlCl_4)_2$ chain. The second benzene (molecule of solvation) lies in a cleft between chains. Assuming that the bound benzene molecule occupies only one coordination site, then the coordination number of Sn(II) is seven with approximately pentagonal bipyramid geometry. Alternately, in the more conventional sense of benzene donating three electron pairs, the coordi-

Table II. Interatomic Distances (Å) and Angles (deg)

	Bonded Distances		
Sn–Cl(1)	3.020 (2)	Sn–Cl(2)	2.907 (2)
Sn–Cl(3')	3.280 (2)	Sn–Cl(4')	3.145 (2)
Sn–Cl(6)	2.881 (2)	Sn–Cl(7)	2.766 (2)
Sn–C(4)	3.05 (1)	Sn–C(5)	3.03 (1)
Sn–C(6)	3.06 (1)	Sn–C(1)	3.08 (1)
Sn–C(2)	3.08 (1)	Sn–C(3)	3.07 (1)
Al(1)–Cl(1)	2.134 (3)	Al(1)–Cl(2)	2.141 (3)
Al(1)–Cl(3)	2.112 (4)	Al(1)–Cl(4)	2.115 (3)
Al(2)–Cl(5)	2.068 (3)	Al(2)–Cl(6)	2.165 (3)
Al(2)–Cl(7)	2.199 (3)	Al(2)–Cl(8)	2.081 (3)
C(4)–C(5)	1.35 (2)	C(5)–C(6)	1.36 (2)
C(6)–C(1)	1.42 (2)	C(1)–C(2)	1.40 (2)
C(2)–C(3)	1.38 (2)	C(4)–C(3)	1.33 (2)
C(10)–C(11)	1.38 (2)	C(11)–C(12)	1.41 (2)
C(12)–C(7)	1.43 (2)	C(7)–C(8)	1.34 (2)
C(8)–C(9)	1.34 (2)	C(9)–C(10)	1.38 (2)

	Selected Nonbonded Distances Less Than 4 Å		
C(4)–Cl(1)	3.72 (1)	C(5)–Cl(2)	3.70 (1)
C(6)–Cl(2)	3.81 (2)	C(1)–Cl(6)	3.87 (1)
C(2)–Cl(3)	3.75 (1)	C(3)–Cl(4)	3.64 (1)
C(1)–Cl(3)	3.81 (1)	C(10)–Cl(2)	3.72 (1)
C(10)–Cl(6)	3.94 (1)	C(11)–Cl(2)	3.70 (1)
C(11)–Cl(5)	3.96 (1)	C(12)–Cl(5)	3.96 (1)
C(11)–Cl(8)	3.93 (1)	C(11)–Cl(7)	3.89 (1)
C(4)–Cl(8)	3.86 (1)	C(12)–Cl(1)	3.91 (1)
C(4)–Cl(5)	3.82 (1)	C(8)–Cl(4)	3.79 (2)
C(9)–Cl(4)	3.77 (1)	C(8)–Cl(1)	3.87 (2)
C(9)–Cl(1)	3.82 (2)	Sn–Ring center	2.74 (1)

	Angles		
Cl(1)–Sn–Cl(2)	68.53 (6)	Cl(2)–Sn–Cl(6)	76.01 (6)
Cl(3)–Sn–Cl(6)	73.86 (6)	Cl(3)–Sn–Cl(4)	63.18 (6)
Cl(1)–Sn–Cl(4)	70.65 (6)	Cl(1)–Sn–Cl(7)	81.14 (7)
Cl(2)–Sn–Cl(7)	81.32 (7)	Cl(6)–Sn–Cl(7)	72.90 (6)
Cl(3)–Sn–Cl(7)	78.37 (7)	Cl(4)–Sn–Cl(7)	80.30 (7)
Cl(1)–Sn–Ring center	101.6 (7)	Cl(2)–Sn–Ring center	101.7 (7)
Cl(3)–Sn–Ring center	98.2 (7)	Cl(4)–Sn–Ring center	98.5 (7)
Cl(6)–Sn–Ring center	105.9 (7)	Cl(7)–Sn–Ring center	176.5 (7)
Cl(1)–Al(1)–Cl(2)	103.0 (1)	Cl(3)–Al(1)–Cl(4)	105.7 (1)
Cl(1)–Al(1)–Cl(4)	111.7 (1)	Cl(2)–Al(1)–Cl(3)	112.9 (1)
Sn–Cl(1)–Al(1)	92.7 (1)	Sn–Cl(2)–Al(1)	95.5 (1)
Cl(5)–Al(2)–Cl(6)	112.3 (2)	Cl(6)–Al(2)–Cl(7)	100.5 (1)
Cl(7)–Al(2)–Cl(8)	109.7 (2)	Cl(5)–Al(2)–Cl(8)	114.7 (2)
		Sn–Cl(3)–Al(1)	90.9 (1)
		Sn–Cl(4)–Al(1)	94.6 (1)

Benzene Ring Angles of Ring Bound to Sn		Benzene Ring Angles of Molecule of Solvation	
C(1)–C(2)–C(3)	120.1 (5)	C(7)–C(8)–C(9)	122.7 (8)
C(2)–C(3)–C(4)	119.4 (6)	C(8)–C(9)–C(10)	119.8 (6)
C(3)–C(4)–C(5)	122.0 (4)	C(9)–C(10)–C(11)	120.8 (5)
C(4)–C(5)–C(6)	122.5 (6)	C(10)–C(11)–C(12)	119.2 (6)
C(5)–C(6)–C(1)	116.8 (7)	C(11)–C(12)–C(7)	118.0 (7)
C(6)–C(1)–C(2)	119.2 (5)	C(12)–C(7)–C(8)	119.3 (6)

nation number would be described as nine. We prefer the former description.

The chlorine atoms Cl(1), Cl(2), Cl(6), Cl(3'), and Cl(4') lie in a plane (Table III) with the tin displaced from this plane by 0.591 (1) Å towards the bound benzene ring. The axial chlorine, Cl(7), is 2.169 (2) Å above this plane. The equatorial Sn–Cl distances range from 2.881 (2) to 3.280 (2) Å (chlorines (1), (2), (6), (3') and (4')) while the axial Sn–Cl distance is shorter at 2.766 (2) Å. These distances are somewhat long when compared to the sum of the respective covalent radii of 2.39 Å,[20] but are considered as real covalent interactions since the sum of the van der Waal's radii is 4.00 Å.[21] Tin–chlorine distances of 2.61 to 3.33 Å have been observed in [Ar–SnCl]$_2$(AlCl$_4$)$_2$[5] where Ar is benzene or p-xylene, while anhydrous stannous chloride contains a Sn–Cl distance of 2.66 Å.[22] Somewhat shorter Sn–Cl distances of 2.59 Å for SnCl$_2$·2H$_2$O[23a] and 2.63 and 2.54 Å for KSnCl$_3$[23b] have also been reported. Two factors are operative to make the Sn–Cl distances long in the present structure, one of which is that they are all

bridging distances but more important is the fact that they are essentially one-electron bonds (vide infra). The Cl(equatorial)–Sn–Cl(equatorial) angles in the present structure vary from 63.18 (6) to 75.01 (6)° while the ideal value for these angles based on a regular pentagon is 72.0°. The smaller values in the series (Cl(1)–Sn–Cl(2), 68.53 (6)°, and Cl(3')–Sn–Cl(4'), 63.18(6)°) occur when the chlorine atoms are bound to the same aluminum atom, and one would expect such a distortion to be observed. Conversely, the larger Cl–Sn–Cl bond angles are found for chlorines bound to different aluminum atoms. It is interesting to note that the Sn–Cl distances and angles and in fact the local metal geometry are very similar to that found for C$_6$H$_6$·U(AlCl$_4$)$_3$.[6] These values appear regardless of the fact that the radius of U^{3+} is approximately 0.2 Å greater than Sn^{2+} [24] (vide infra).

The tin–carbon distances average 3.06 (1) Å with individual deviations of ±0.03 Å or less, indicating a symmetrical interaction between tin and benzene. The tin-to-ring center distance is 2.74 (1) Å with a (ring center)–Sn–Cl(7)
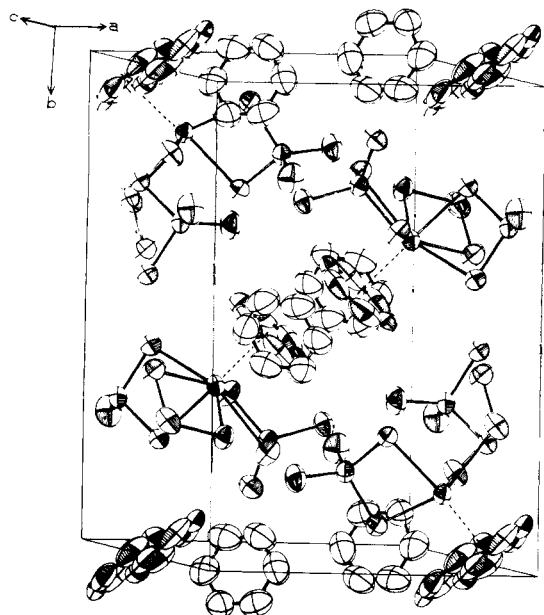
Figure 2. Packing of atoms in the unit cell between the limits $a = 1.2$ unit cell, $b = 1.2$ unit cell, $c = 1.0$ unit cell in the respective directions. The origin of the unit cell is in the upper front left-hand corner of the volume enclosed by solid lines. The dotted line represents the Sn to center of bound benzene ring. The benzene ring bound to Sn is denoted by cut-away cross-hatched atoms, whereas the benzene rings of solvation are plain ellipses.

Table III

Equation of Least-Squares Plane of the Type[a]

$$Ax + By + Cz - D = 0$$

$A = 0.6437$,	$B = 0.7512$,	$C = -0.1463$,	$D = 4.9856$

Deviation of Atoms from the Least-Squares Plane, Å

Cl(1)	0.070 (3)	Cl(2)	-0.095 (2)
Cl(3)	-0.076 (3)	Cl(4)	-0.010 (2)
Cl(6)	0.098 (2)		

Deviation of Atoms Not Included in the Least-Squares Plane, Å

Sn	-0.591 (1)	Cl(7)	2.169 (2)

$A = 0.6679$,	$B = 0.7244$,	$C = -0.1706$,	$D = 1.7007$

Deviation of Atoms from the Least-Squares Plane, Å

C(4)	-0.005 (11)	C(5)	-0.000 (12)
C(6)	0.008 (16)	C(1)	-0.008 (13)
C(2)	0.001 (13)	C(3)	0.006 (14)

$A = -0.4572$,	$B = -0.2864$,	$C = -0.8420$,	$D = 3.2147$

Deviation of Atoms from the Least-Squares Plane, Å

C(10)	0.002 (15)	C(11)	-0.011 (14)
C(12)	0.019 (14)	C(7)	-0.018 (16)
C(8)	0.004 (17)	C(9)	0.004 (15)

[a] x, y, and z refer to internal orthogonal coordinate system ("International Tables for X-Ray Crystallography", Vol. II, The Kynoch Press, Birmingham, England, 1967, p 61).

Table IV. Root-Mean-Square Displacements along Principal Axes of the Thermal Ellipsoid, Å

Atom	Axis 1	Axis 2	Axis 3
Sn	0.198 (1)	0.227 (1)	0.246 (1)
Cl(1)	0.199 (3)	0.241 (3)	0.335 (3)
Cl(2)	0.208 (3)	0.225 (3)	0.331 (3)
Cl(3)	0.242 (3)	0.264 (3)	0.305 (3)
Cl(4)	0.203 (3)	0.247 (3)	0.295 (3)
Cl(5)	0.229 (3)	0.305 (3)	0.367 (4)
Cl(6)	0.235 (3)	0.242 (3)	0.289 (3)
Cl(7)	0.226 (3)	0.234 (3)	0.269 (3)
Cl(8)	0.209 (3)	0.321 (3)	0.340 (3)
Al(1)	0.191 (3)	0.223 (3)	0.249 (3)
Al(2)	0.204 (3)	0.230 (3)	0.258 (3)
C(1)	0.217 (15)	0.265 (15)	0.520 (22)
C(2)	0.208 (15)	0.245 (15)	0.539 (21)
C(3)	0.197 (15)	0.274 (15)	0.465 (18)
C(4)	0.193 (13)	0.285 (14)	0.417 (16)
C(5)	0.203 (14)	0.297 (15)	0.435 (18)
C(6)	0.232 (16)	0.319 (16)	0.463 (20)
C(7)	0.285 (16)	0.319 (16)	0.419 (19)
C(8)	0.288 (17)	0.345 (17)	0.404 (19)
C(9)	0.276 (16)	0.322 (17)	0.410 (18)
C(10)	0.260 (16)	0.337 (15)	0.388 (17)
C(11)	0.298 (15)	0.309 (14)	0.345 (15)
C(12)	0.281 (16)	0.341 (16)	0.379 (16)

angle of 176.5 (7)°. The ideal bond angle for pentagonal bipyramid geometry would be 180°. These metal-to-carbon distances seem to be long when compared to ruthenocene (Ru–C = 2.21 (2) Å)[25] or other metal–carbon distances found in transition metal complexes,[26] but again they are shorter than the sum of the van der Waal's radii of 4.00 Å.[21] The displacement of the tin from the plane containing the five chlorine atoms (Table III) towards the benzene ring is thought to arise from the steric constraints imposed by the chelated AlCl$_4^-$ groups and the van der Waal's repulsion between the chlorine and carbon atoms. Examination of the carbon–chlorine nonbonded distances shows two different types of distances. The first type of interaction arises from the bound benzene ring (carbon atoms 1, 2, 3, 4, 5, and 6) and the five chlorine atoms that lie in a plane (chlorine atoms 1, 2, 3', 4', and 6). The second type of nonbonded interaction would result from the benzene molecule of

solvation and all other chlorines. Nonbonded interactions of the first type average 3.76 (1) Å while interactions of the second type are at least 0.09 Å longer at 3.85 (1) Å. Thus, we view the long tin–carbon distances (in part) as the direct result of steric repulsions between the carbon and chlorine atoms and the constraints of molecular packing (vide infra).

The bond distances and angles for the tetrachloroaluminate ions and the benzene rings show the expected values. Both benzene molecules are planar within experimental error (Table III).

Discussion

Any discussion of the chemical bonding between Sn(II) and its neighboring atoms must rationalize the following facts: (1) the relatively long Sn–Cl distances; (2) the local C_{6v} symmetry of the Sn–benzene interaction; (3) the relatively long Sn–C distances; (4) the similarity of the present structure, in terms of local geometry, to that of $C_6H_6U(AlCl_4)_3$.[6] We outline here one possible description of the bonding in terms of a qualitative molecular orbital scheme. A qualitative molecular orbital energy level diagram can be easily constructed and is shown in Figure 3. For the sake of simplicity and to define readily recognizable symmetry molecular orbitals, we have assumed C_{5v} symmetry. This is not the correct symmetry about Sn(II), but that would only change details and not the overall picture of the bonding. Although d orbitals are frequently used in the description of bonding in higher coordination numbers (>6), we have not made use of them because the 5d levels are approximately 19.1 eV[27] above the 5s compared to 9.1 eV for the 5s–5p separation. The inclusion of these d orbitals again would not materially affect the description. Sn–Cl π bonding is neglected as well in this discussion.

This arrangement of levels is very easily conceived by analogy with the dibenzene complexes, e.g., dibenzenechromium.[28] The two lowest and two highest levels on the left in Figure 3 are the usual one-electron benzene molecular orbitals. The six appropriate linear combinations of the chlorine σ orbitals (e_1, e_2, $2a_1$) are then between the bonding and antibonding benzene levels (Figure 3).

The molecular orbitals for the benzene, Sn(II), and six chlorines then order in a straightforward pattern. Clearly, the a_1, mostly benzene in character, lies lowest in energy,

followed by e_1 which is the principal bonding between Sn(II) and benzene. The next grouping of energy levels contains those between chlorine and Sn(II) with most likely the totally symmetric a_1 MO's being lowest. One of these is the Sn(5p)–Cl σ axial interaction while the other is a totally symmetric framework MO involving the Sn(II) (5s) and the equatorial halogen σ orbitals. e_1' involves the Sn(II) $5p_x$, $5p_y$, and halogen σ orbitals whereas e_2 is a nonbonding MO involving only chlorine. The next level is a_1''', probably mostly Sn(II) 5s in character. The remaining levels are all antibonding. The 20 electrons then fill these levels through and including a_1''', leading to a diamagnetic closed shell electronic structure. We make no claim as to the uniqueness of the ordering of these molecular energy levels, but it is quite clear that they would fall into four groups: (1) a_1e_1; (2) a_1', a_1'', e_1'; (3) e_2; (4) a_1'''. In addition, it is to be noted that this ordering of energy levels makes a_1''' almost pure metal 5s in character. This point of view is in agreement with the fact that the Mössbauer spectra yields a single line with an isomer shift of 3.93 ± 0.1[29] relative to a BaSnO$_3$ source. SnSO$_4$ and Sn(SbF$_6$)$_2$ have isomer shifts of 4.3 and 4.44 on this same scale. Clearly the 5s electrons are in an almost spherical environment as in Sn(II) in Sn(SbF$_6$)$_2$. This isomer shift with no quadrupole splitting is also in agreement with the long (weak) Sn–Cl bonds observed in the structure of this compound.

Since the principal interaction between Sn(II) and benzene involves the e_1 MO which is overlap between p orbitals lying in a plane parallel to the benzene ring, it is not surprising that the Sn–C distance is long. Furthermore, the interaction between $5p_x$, $5p_y$, and benzene e_1 would give rise to the C_{6v} Sn(II)–C$_6$H$_6$ complex. In contrast, the strongest bonding interaction in ferrocene-type compounds is a d orbital directed toward the carbon atoms of the aromatic. Since only the a_1', a_1'', and e_1' are Sn–Cl bonding MO's, that means that there are only eight bonding electrons for six chemical bonds and these Sn–Cl bonds must be long in comparison to normal Sn–Cl single bonds.

The bonding in C$_6$H$_6$·U(AlCl$_4$)$_3$[6] can also be understood by a simple modification of Figure 3. It is generally assumed with π complexes of the actinides that the f → d orbital separation is such that d orbital interaction is not important.[30] We shall assume likewise even though the f → d separation for U^{3+} is about 3.7 eV and less than the s → p separation of Sn^{2+}. In addition, we will neglect to the first approximation the use of U^{3+} s and p orbitals. Hence, the interaction between U^{3+} and benzene and chloride will be discussed only in terms of 5f orbitals. Under C_{5v} the sevenfold degenerate f orbitals of the free atom decompose into the irreducible representations a_1, e_1, and $2e_2$. If the simple pictoral combinations as indicated by Friedman et al.[31] are used then: f_{z^3} belongs to a_1, $f_{xz^2}f_{zy^2}$ to e_1, $f_{xyz}f_{z(x^2-y^2)}$ to e_2 and $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$ also to e_2. It is immediately clear by reference to Figure 3 that the halogen nonbonding e_2 orbital becomes a bonding molecular orbital primarily with e_2 ($f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$ with some smaller mixing of f_{xyz}, $f_{z(x^2-y^2)}$). Therefore, we add four more bonding electrons into the equatorial plane for π-C$_6$H$_6$·U(AlCl$_4$)$_3$ than for the π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$, and this, at least in part, compensates for the fact that U^{3+} is larger than Sn^{2+}; yet the M–Cl distances are essentially the same in the two compounds. The use of inner f orbitals for U^{3+} and outer p in Sn^{2+} contributes to this bond length similarity. The lowest bonding a_1 and e_1 levels for the U^{3+} system then involve f_{z^3} and f_{xz^2}, f_{yz^2} and are the principal benzene → metal bonding molecular orbitals. These are better directed than the Sn 5s, 5p orbitals and account for the similarity in the M–C distances. Of course, any interaction between e_1 d orbitals (d_{xz}, d_{yz}) would contribute to the stabilization of the U–C
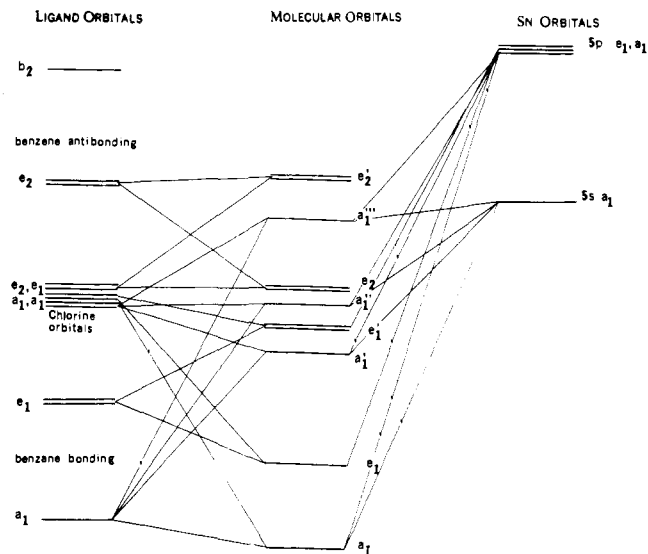

Figure 3. A qualitative molecular orbital energy level diagram for the interaction of Sn(II) with the seven ligands: six Cl and one benzene. The ordering of the MO levels involving halogen may be different from that depicted, but it would not change the arguments in the text. The antibonding levels above e_2' have not been included for the sake of simplicity. For the same reason some lines have been excluded. The 5d levels of Sn(II) on this scale would be off the figure.

bonds as well. The remainder of the energy levels in Figure 3 would be the same with the appropriate replacement of metal 5f for metal 5s, 5p.

The description of the bonding in π-C$_6$H$_6$Sn(AlCl$_4$)$_2$·C$_6$H$_6$ points out the fundamental differences in bonding between Ag(I), Cu(I), Sn(II), and Pb(II) aromatics and the ferrocene-type structures; i.e., the binding due to the interaction of the partially filled d shell with the aromatic is lost with the post-transition-metal ions regardless of the geometry of the final complex.

Although the chemical binding and geometry of the present Sn(II) species are very similar to those of the corresponding Pb(II) moiety, there are significant differences in the chemistry. For example, at lower temperatures under carefully controlled conditions from SnCl$_2$, AlCl$_3$, and benzene-p-xylene, [π-ArSnCl]$_2$(AlCl$_4$)$_2$ is obtained.[6] This material contains a halogen bridged dimer, formally Sn$_2$Cl$_2^{2+}$. On the other hand, in the analogous reaction between PbCl$_2$, AlCl$_3$, and the same aromatics as above, no such product is obtained but eventually only, e.g., π-C$_6$H$_6$-Pb(AlCl$_4$)$_2$·C$_6$H$_6$.[1] This result could be rationalized on the basis that substantial Sn–Cl covalent bonding exists in SnCl$_2$(s)[22] whereas PbCl$_2$(s) is much more appropriately discussed as an ionic structure composed of Pb^{2+} with nine Cl$^-$ neighbors in the geometry of a tricapped trigonal prism.[32]

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FSGO Investigation of Several Conformers of Cyclohexane

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Abstract: Four conformations of cyclohexane have been theoretically calculated by the ab initio floating spherical Gaussian orbital model (FSGO). The order of energies is as expected but the energy differences are exaggerated as has previously been found in other ring systems and rotational barriers.

In this paper, we wish to report the results of an investigation of the geometry of four conformations of cyclohexane, chair (D_{3d}), boat (C_{2v}), half-chair (C_2), and planar (D_{6h}), by means of the FSGO (floating spherical Gaussian orbital) model. The FSGO model makes use of an absolute minimum basis set, where each orbital is doubly occupied. As currently applied, the model predicts the electronic and geometric structure of singlet ground states of molecules with local orbitals without the use of any arbitrary or semi-empirical parameters. The local orbitals are constructed by using single normalized spherical Gaussian functions

$$\Phi(\mathbf{r} - \mathbf{R}_i) = (2/\pi\rho_i^2)^{3/4} \exp[-(\mathbf{r} - \mathbf{R}_i)^2/\rho_i^2]$$

with orbital radius ρ_i and position $\mathbf{R}_i$. A single Slater determinant represents the total electronic wave function. The total energy can be minimized by a direct search procedure with respect to all parameters: orbital radii, ρ_i, orbital positions, $\mathbf{R}_i$, and nuclear positions. The advantage of the FSGO model as described above is that no SCF iterations are required. This model has been used previously for small ring systems and other small hydrocarbon molecules with some success,[1] particularly in the area of geometry optimization.

Unless otherwise indicated, the geometrical parameters for the chair, boat, and planar conformations were those of their ideal representations. All C–C and C–H bond lengths were assumed equal at 1.54 and 1.10 Å, respectively, for all calculations. The bond angles and the dihedral angles for the half-chair conformation were taken from the empirical conformational study of Hendrickson.[2] For the half-chair and planar conformations, all H–C–H angles were set equal to 107.5°. The results are shown in Table I.

It has been known for quite some time that the equilibrium ground-state conformation of cyclohexane is a slightly flattened version of the chair conformation rather than an ideal chair with C–C–C bond angles of 109.47°. The bond angle has been experimentally determined to be 111.05–111.55°.[9,10] It is calculated to be 111.13° by the FSGO model. This angle and other geometrical quantities are determined by fitting to a parabola the three calculated points closest to the energy minimum of the particular surface under examination.

There are four coplanar carbon atoms in the half-chair conformation. This gives rise to considerable eclipsing of the hydrogens of neighboring methylene groups. The FSGO model calculations indicate that a slight "rocking" of these