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Metal Ion–Aromatic Complexes. 24. Synthesis and Crystal Structure of Chloro(π-aryl)tin(II) Tetrachloroaluminate Containing the $Sn_2Cl_2^{2+}$ Moiety

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The compounds π-ArClSn($AlCl_4$) in which Ar = p-$(CH_3)_2C_6H_4$ (I) or C_6H_6 (II) have been prepared and their crystal structures determined. Both structures contain the $Sn_2Cl_2^{2+}$ dimeric unit as an integral feature. The crystal structures are composed of these dimers interconnected by bridging $AlCl_4^-$ groups to form infinite-chain structures in the [001] directions. The Sn–Cl distances in the dimer are approximately 2.6 Å (an expected Sn^{2+}–Cl single-bond distance). The coordination polyhedron of Sn^{2+} is completed by interactions with adjacent $AlCl_4^-$ groups and an interaction with the π orbitals of the aromatic moiety to give a distorted octahedron. The Sn^{2+} lies on the line perpendicular to the aromatic ring and passing through its center with approximately equal Sn–C bond distances. The Sn–C and Sn–Cl bonding is discussed relative to π-$C_6H_6Sn(AlCl_4)_2\cdot C_6H_6$. The following crystal data were obtained: p-$(CH_3)_2C_6H_4ClSn(AlCl_4)$ (I): space group $I2/c$; $Z = 8$, $\rho_{calcd} = 1.86$ g cm^{-3}, $\rho_{obsd} \approx 1.7$ g cm^{-3}; $a = 18.970$ (7) Å, $b = 10.903$ (4) Å, $c = 15.470$ (4) Å; $\beta = 107.33$ (1)°; number of observations in solution and refinement of structure = 2476; final $R = 0.0490$. $C_6H_6ClSn(AlCl_4)$ (II): space group $P2_1/n$; $Z = 4$; $\rho_{calcd} = 2.02$ g cm^{-3}, $\rho_{obsd} = 2.1$ g cm^{-3}; $a = 19.624$ (6) Å, $b = 9.531$ (1) Å, $c = 7.099$ (1) Å; $\beta = 93.65$ (1)°; number of observations used in solution and refinement of structure = 2446; final $R = 0.070$. Both structures were refined by full-matrix least squares using diffractometer data with anisotropic temperature factors, and anomalous dispersion corrections for Sn, Al, and Cl were included.

Introduction

The interaction of acceptor metal ions with donor aromatic molecules has been the object of interest for a number of years.[2] These donor–acceptor complexes are interesting not only because of the nature of the chemical binding between donor and acceptor but also because of the fact that appropriate members of this series have solution properties which indicate that they may act as carriers for aromatics,[3-5] low molecular weight olefins, and small molecules such as CO and NO.[4]

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-ArSn$(AlCl_4)_2\cdot$Ar[2b,6] and (2) π-ArClSn($AlCl_4$),[7] a dimer containing halogen-brided Sn(II). We report here the details of the preparations of π-$C_6H_6ClSn(AlCl_4)$ and π-$(CH_3)_2C_6H_6ClSn(AlCl_4)$ and the crystal structure determinations, and we give an interpretation of the bonding.

Experimental Section

Preparation of π-ArClSn($AlCl_4$). Anhydrous stannous chloride (8 g, 44 mmol) and aluminum chloride (10 g, 75 mmol) were placed in one arm of an H-tube. Benzene or p-xylene (50 mL, distilled from CaH_2 under nitrogen atmosphere) was placed in the other arm. After being degassed, it was distilled onto the $SnCl_2$–$AlCl_3$ mixture by immersing one arm of the H-tube in a liquid nitrogen trap.[8,9] The reaction mixture was allowed to come to room temperature and then heated for 1 h in an oil bath at 50 °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 the excess solvent. The crystals were coated with petroleum jelly and sealed in Lindemann capillaries to prevent decomposition by water vapor and loss of aromatic character.

Heating the reaction mixture at 80 °C for 2.5 h gives a compound of the formula ArSn$(AlCl_4)_2\cdot$Ar.[2b,6]

X-ray Data

p-$(CH_3)_2C_6H_4ClSn(AlCl_4)$, I. Preliminary Weissenberg and precession film data showed the crystals to have the systematic absences $h + k + l = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, indicating the centric, noncentric pair $I2/c$, Ic.[10a] With eight molecules per unit cell the calculated density is 1.86 g cm^{-3}, while the observed density is 1.8 ± 0.1 g cm^{-3}. A more accurate value was unobtainable because the crystals rapidly decomposed in halocarbon solutions.

A single crystal with dimensions 0.15 × 0.30 × 0.66 mm was mounted along the [112] direction and aligned on a full-circle Picker automated diffractometer by a local variation of well-known methods.[11] The cell constants were determined by least-squares refinement of the angles χ, ϕ, and 2θ for 11 general hkl reflections.[11] The cell constants are $a = 18.970$ (7) Å, $b = 10.903$ (4) Å, $c = 15.470$ (4) Å, and $\beta = 107.31$ (1)°. A total of 4668 independent intensity data were collected with unfiltered Mo Kα radiation;[12] λ was 0.710 68 Å to 2θ of 60°. Reflections were considered absent if the net intensity was less than $2.5[2.095(B_1 + B_2)]^{1/2}$. By this criterion 2464 reflections were retained as being nonzero. For 20 of the hkl reflections in which Kα and Kβ radiation overlapped, a Zr filter was used. Backgrounds were measured at ±0.70°, 2θ from the peak maximum for 20 s, and the peaks were scanned for 83.80 s (1.4°, 2θ) by the usual θ–2θ scan technique. A standard reflection (864) was measured every 10 reflections to monitor the stability of the operation.[13] An ω scan was taken of the standard peak and the half-width spread at half-width height was measured to establish the mosaic spread of the crystal. The half-width spread was no more than 0.13° which indicated that the entire peak was scanned for each reflection. The variation in the standard reflection from one standard to the next was no more than 2% of the total scan intensity or less than $\sigma[I(\text{net})]$. From the beginning to the end of the data collection the standard peak showed a total loss in intensity from decomposition of approximately 10% and the data were scaled to compensate for this variation.

With a linear absorption coefficient, μ, of 25.52 cm^{-1} the minimum and maximum transmission coefficients of a crystal, bound by the planes of the forms {100}, {011}, and {112}, were 0.782 and 0.471, respectively. The counting rate never exceeded 5000 counts/s and no attenuators were used. The pulse height analyzer was set such that 90% of the scattered radiation was counted; Lorentz–polarization corrections were made and the intensities were reduced to structure factors.

$C_6H_6ClSn(AlCl_4)$, II. Preliminary Weissenberg and precession photographic data, $hk0$, $hk1$, ..., $hk6$, $h0l$, $0kl$, 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 $P2_1/n$.[10b]

A single crystal of dimensions 0.33 × 0.43 × 0.70 mm was mounted with the long direction approximately parallel to the ϕ axis on a card-controlled Picker full-circle automatic diffractometer and aligned as above[11] for I.

A least-squares fit of the χ, ϕ, and 2θ angles of 14 reflections accurately centered on the diffractometer was used to determine the lattice constants at 23–25 °C (λ 0.710 68 Å for Mo Kα radiation); $a = 19.624$ (6) Å, $b = 9.531$ (1) Å, $c = 7.099$ (1) Å, $\beta = 93.65$ (1)°. With $Z = 4$ the calculated density is 2.02 g cm^{-3}, while the observed density is between 2.0 and 2.2 g cm^{-3}. A more accurate value was unobtainable because the crystals decompose very rapidly in halocarbon solution. The linear absorption coefficient μ was calculated to be 27.3 cm^{-1} with Mo Kα radiation. With this μ, the above crystal dimensions, and the faces of the forms {100}, {010}, {110}, and {421}, the variation in transmission coefficient was found to be 0.471–0.503.[14] A total of 2908 independent hkl reflections were measured by θ–2θ scan

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Table I. Final Positional and Thermal Parameters[a, b]

(a) $p\text{-}(CH_3)_2C_6H_4ClSn(AlCl_4)$

atom	x	y	z
Sn	0.3371 (1)	0.6818 (1)	0.2136 (1)
Cl(1)	0.2268 (2)	0.8342 (3)	0.1536 (2)
Cl(2)	0.6063 (2)	0.8294 (4)	0.4324 (2)
Cl(3)	0.4712 (2)	0.6029 (3)	0.3868 (3)
Cl(4)	0.4717 (2)	0.8339 (4)	0.5445 (3)
Cl(5)	0.4202 (2)	0.8910 (3)	0.3107 (2)
Al	0.4943 (2)	0.7912 (3)	0.4237 (3)
C(1)	0.2676 (7)	0.5403 (11)	0.0365 (9)
C(2)	0.3390 (7)	0.4959 (12)	0.0516 (9)
C(3)	0.3714 (8)	0.4205 (12)	0.1302 (11)
C(4)	0.3335 (9)	0.3927 (12)	0.1935 (9)
C(5)	0.2631 (8)	0.4392 (12)	0.1759 (10)
C(6)	0.2302 (7)	0.5102 (13)	0.0999 (9)
C(7)	0.2334 (8)	0.6204 (15)	−0.0446 (9)
C(8)	0.3687 (12)	0.3128 (16)	0.2681 (11)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	22 (0)	66 (1)	42 (0)	3 (0)	8 (0)	7 (1)
Cl(1)	29 (1)	84 (3)	38 (1)	−7 (1)	10 (1)	−11 (2)
Cl(2)	20 (1)	131 (4)	66 (2)	−5 (2)	9 (1)	−3 (2)
Cl(3)	30 (1)	79 (3)	114 (3)	2 (2)	−2 (2)	−14 (3)
Cl(4)	49 (2)	165 (5)	56 (2)	8 (2)	22 (1)	5 (3)
Cl(5)	27 (1)	79 (3)	49 (2)	−5 (1)	5 (1)	−5 (2)
Al	21 (1)	86 (4)	48 (2)	−2 (2)	7 (1)	−12 (2)
C(1)	31 (4)	71 (11)	53 (7)	−8 (6)	12 (5)	−27 (7)
C(2)	26 (4)	86 (12)	55 (7)	−3 (6)	10 (4)	−22 (8)
C(3)	33 (5)	65 (11)	86 (10)	0 (6)	6 (6)	−31 (9)
C(4)	52 (6)	77 (12)	45 (8)	−24 (8)	3 (6)	−2 (8)
C(5)	40 (6)	80 (12)	61 (8)	−24 (7)	13 (6)	−22 (9)
C(6)	23 (4)	107 (14)	54 (7)	−19 (6)	12 (4)	−29 (9)
C(7)	44 (6)	142 (17)	40 (7)	6 (9)	−11 (5)	−4 (10)
C(8)	83 (11)	112 (18)	129 (16)	−19 (11)	−5 (11)	58 (15)

(b) $C_6H_6ClSn(AlCl_4)$

atom	x	y	z
Sn	0.0869 (1)	0.0946 (1)	0.0988 (2)
Cl(1)	0.0266 (2)	0.3345 (5)	−0.0797 (6)
Cl(2)	0.1813 (2)	0.2223 (5)	−0.2043 (7)
Cl(3)	0.1377 (3)	0.5741 (5)	−0.2762 (7)
Cl(4)	0.0582 (3)	0.3212 (6)	−0.5592 (7)
Cl(5)	0.0372 (2)	−0.0341 (5)	−0.2048 (5)
Al	0.1022 (2)	0.3688 (5)	−0.2888 (7)
C(1)	0.2038 (13)	−0.1243 (24)	0.0811 (27)
C(2)	0.1486 (11)	−0.1979 (22)	0.1506 (32)
C(3)	0.1308 (12)	−0.1679 (23)	0.3274 (29)
C(4)	0.1720 (14)	−0.0689 (26)	0.4497 (32)
C(5)	0.2267 (9)	−0.0063 (22)	0.3691 (30)
C(6)	0.2426 (10)	−0.0266 (27)	0.1809 (33)

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	20 (0)	68 (1)	161 (2)	0 (1)	6 (2)	2 (2)
Cl(1)	25 (1)	78 (5)	234 (10)	9 (2)	29 (3)	10 (6)
Cl(2)	21 (1)	110 (6)	276 (11)	8 (2)	23 (3)	24 (7)
Cl(3)	44 (2)	80 (6)	257 (12)	−20 (3)	1 (4)	14 (6)
Cl(4)	50 (2)	170 (9)	195 (11)	11 (4)	−24 (4)	−81 (8)
Cl(5)	24 (1)	98 (5)	153 (8)	8 (2)	14 (2)	29 (5)
Al	23 (1)	65 (5)	143 (10)	−3 (2)	6 (3)	9 (6)
C(1)	58 (9)	157 (40)	201 (48)	−44 (15)	44 (17)	−6 (3)
C(2)	35 (7)	98 (26)	372 (68)	−3 (11)	0 (18)	42 (34)
C(3)	43 (9)	125 (30)	266 (55)	−9 (14)	31 (18)	−55 (34)
C(4)	54 (11)	149 (39)	241 (60)	−2 (17)	−40 (21)	−74 (40)
C(5)	19 (5)	142 (31)	297 (53)	2 (10)	−6 (13)	−40 (34)
C(6)	26 (6)	188 (39)	352 (65)	2 (13)	23 (16)	−30 (43)

[a] Esd's of the last figure are given in parentheses. [b] Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$.

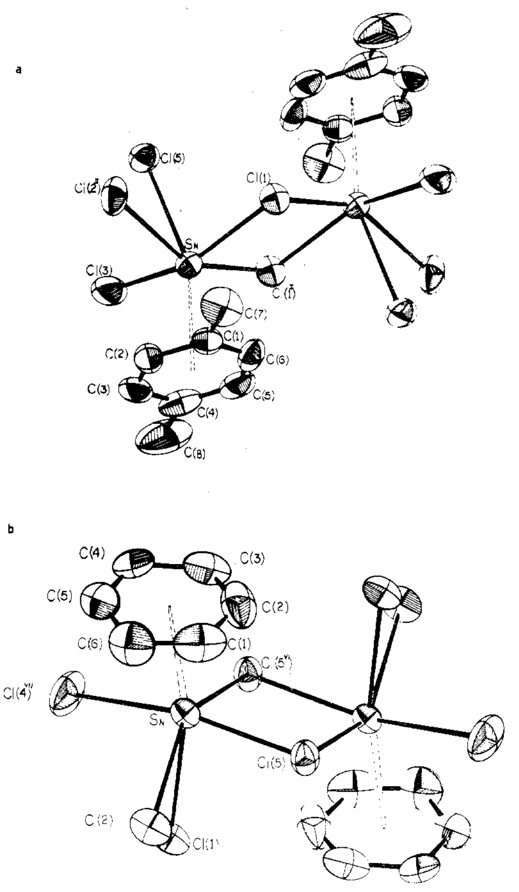

Figure 1. (a) ORTEP[31] drawing of the local environment about the $Sn_2Cl_2^{2+}$ dimer in $p\text{-}(CH_3)_2C_6H_4ClSn(AlCl_4)$. All bonded atoms to each Sn are shown as solid lines except the tin–aromatic interaction which is shown as a dotted line to the center of the ring. The atom notation is as in the text. Since the center of $Sn_2Cl_2^{2+}$ moiety is on a crystallographic center of symmetry (for simplicity), only half of the atoms are labeled. Ellipsoids are drawn at the 50% probability level. (b) As in (a), but for $C_6H_6ClSn(AlCl_4)$.

techniques to $2\theta = 60°$ with unfiltered Mo Kα radiation at 23–25 °C for 108 s at 0.017°/s, and background counts were made for 40 s (B_1 and B_2). Reflections were considered absent if the net intensity was less than $3[2.70(B_1 + B_2)]^{1/2}$. By this criterion 2446 reflections were retained as being nonzero. A standard general reflection was measured every 10th reflection to ensure stability of operation and to monitor any crystal decomposition. No decomposition of the crystal was observed during data collection. The variation from one measurement of the standard reflection to the next was well within counting statistics, $\sigma[I(\text{net})] = [I(\text{scan}) + 2.700^2(B_1 + B_2)]^{1/2}$. 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 diffractometer constants were as above. The half-width at half-peak height of an average reflection was 0.19° at a takeoff angle of 3.7°, indicating a mosaic spread such that all of the reflection is counted during the 1.8° scan. All other factors were the same for I and II.

Structure Solution

$p\text{-}(CH_3)_2C_6H_4ClSn(AlCl_4)$, I. The structure was solved by standard heavy-atom methods.[15] A full-matrix isotropic least-squares refinement converged to an R of 0.108. A full-matrix fully anisotropic least-squares refinement[16] after three cycles converged to an R of 0.0490 and a weighted R[17] of 0.0686 with 136 variables. On the final cycle of refinement the parameter shifts were less than 0.1 standard deviation. A difference electron density map was qualitatively featureless as is to be expected when the crystal is coated with petroleum jelly in a capillary and some decomposition of $AlCl_4^-$ is always present.

The function minimized was $\sum w(F_o - F_c)^2$ with weights determined by counting statistics.[18] Scattering factors for Sn^{2+}, Cl^-, Al^{3+}, and neutral carbon were from Cromer and Waber.[19] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[20] the values for $\Delta f'$ and $\Delta f''$ for tin, chlorine, and aluminum are those given by Cromer.[21] The final tabulation of observed and calculated structure factors is found elsewhere.[22] Unobserved data were not used in the structure refinement but are listed with the calculated structure factors. Final atomic positional and thermal parameters are in Table Ia. Interatomic distances and

Table II. Interatomic Distances (A) and Angles (deg)[a]

(a) p-$(CH_3)_2C_6H_4ClSn(AlCl_4)$							
Bonded Distances							
Sn–Cl(1)	2.616 (3)	Sn–C(2)	3.23 (1)	Al–Cl(4)	2.091 (5)	C(3)–C(4)	1.41 (2)
Sn–Cl(1$^{\mathrm{I}}$)[b]	2.684 (3)	Sn–C(3)	3.27 (2)	Al–Cl(2)	2.128 (5)	C(4)–C(5)	1.38 (2)
Sn–Cl(5)	2.921 (3)	Sn–C(4)	3.17 (1)	Al–Cl(3)	2.141 (5)	C(5)–C(6)	1.39 (2)
Sn–Cl(2$^{\mathrm{II}}$)	3.208 (3)	Sn–C(5)	2.97 (1)	Al–Cl(5)	2.180 (5)	C(1)–C(6)	1.41 (2)
Sn–Cl(3)	3.214 (4)	Sn–C(6)	2.92 (1)	C(1)–C(2)	1.39 (2)	C(1)–C(7)	1.51 (2)
Sn–C(1)	3.08 (1)			C(2)–C(3)	1.45 (2)	C(4)–C(8)	1.44 (2)
Selected Nonbonded Distances							
Sn–Sn$^{\mathrm{I}}$	4.077 (2)	Cl(1)–C(7$^{\mathrm{III}}$)	3.73 (2)	Cl(4)–C(7$^{\mathrm{I}}$)	3.92 (2)	Cl(2)–C(7$^{\mathrm{II}}$)	3.78 (2)
Sn–C(7)	3.95 (2)	Cl(1)–C(2$^{\mathrm{III}}$)	3.52 (2)	Cl(5)–C(6$^{\mathrm{I}}$)	3.68 (2)	Cl(2)–C(1$^{\mathrm{II}}$)	3.90 (2)
Sn–C(8)	4.12 (2)	Cl(1)–C(5$^{\mathrm{I}}$)	3.58 (2)	Cl(5)–C(5$^{\mathrm{I}}$)	4.00 (2)	Cl(2)–C(7$^{\mathrm{IV}}$)	3.94 (2)
Sn–(COR)[c]	2.77	Cl(1)–C(6)	3.63 (2)	Cl(2)–Cl(3)	3.476 (5)	Cl(3)–Cl(5)	3.392 (5)
Cl(1)–Cl(1$^{\mathrm{I}}$)	3.387 (4)	Cl(1)–C(1$^{\mathrm{III}}$)	3.73 (1)	Cl(2)–Cl(4)	3.488 (5)	Cl(3)–Cl(4)	3.504 (5)
Cl(1)–Cl(3$^{\mathrm{I}}$)	3.682 (4)	Cl(1)–C(1)	3.87 (1)	Cl(2)–Cl(5)	3.535 (5)	Cl(3)–C(2$^{\mathrm{II}}$)	3.63 (2)
Cl(1)–Cl(2$^{\mathrm{II}}$)	3.784 (4)	Cl(4)–Cl(5)	3.772 (5)	Cl(2)–Cl(5$^{\mathrm{II}}$)	3.705 (5)	Cl(3)–C(3$^{\mathrm{II}}$)	3.66 (2)
Cl(1)–Cl(5)	3.800 (4)	Cl(4)–C(3$^{\mathrm{V}}$)	3.82 (2)	Cl(2)–C(6$^{\mathrm{I}}$)	3.54 (2)	Cl(3)–C(8)	3.88 (2)
Cl(1)–Cl(5$^{\mathrm{I}}$)	3.874 (4)	Cl(4)–C(8$^{\mathrm{VI}}$)	3.86 (2)	Cl(2)–C(2$^{\mathrm{II}}$)	3.77 (2)		
Cl(1)–C(7)	3.88 (2)			Cl(2)–C(1$^{\mathrm{IV}}$)	3.78 (2)		
Angles							
Cl(1)–Sn–Cl(1$^{\mathrm{I}}$)	79.43 (9)	Cl(5)–Sn–Cl(2$^{\mathrm{II}}$)	74.2 (1)	Cl(2)–Al–Cl(3)	109.0 (2)	C(2)–C(3)–C(4)	122 (1)
Cl(1)–Sn–Cl(5)	86.48 (9)	Cl(5)–Sn–Cl(3)	66.9 (2)	Cl(2)–Al–Cl(5)	110.3 (2)	C(3)–C(4)–C(5)	117 (1)
Cl(1)–Sn–Cl(2$^{\mathrm{II}}$)	80.34 (9)	Cl(2$^{\mathrm{II}}$)–Sn–Cl(3)	111.9 (1)	Cl(3)–Al–Cl(5)	103.4 (2)	C(3)–C(4)–C(8)	118 (2)
Cl(1)–Sn–Cl(3)	144.71 (9)	Cl(4)–Al–Cl(2)	111.5 (2)	C(2)–C(1)–C(6)	118 (1)	C(5)–C(4)–C(8)	125 (2)
Cl(1$^{\mathrm{I}}$)–Sn–Cl(5)	87.36 (9)	Cl(4)–Al–Cl(3)	111.8 (3)	C(2)–C(1)–C(7)	120 (1)	C(4)–C(5)–C(6)	122 (1)
Cl(1$^{\mathrm{I}}$)–Sn–Cl(2$^{\mathrm{II}}$)	153.34 (9)	Cl(4)–Al–Cl(5)	110.5 (2)	C(6)–C(1)–C(7)	122 (1)	C(5)–C(6)–C(1)	122 (1)
Cl(1$^{\mathrm{I}}$)–Sn–Cl(3)	76.7 (1)			C(1)–C(2)–C(3)	119 (1)		
(b) $C_6H_6ClSn(AlCl_4)$							
Bonded Distances							
Sn–Cl(1)	2.837 (4)	Sn–C(2)	3.05 (2)	Al–Cl(1)	2.189 (6)	C(2)–C(3)	1.36 (3)
Sn–Cl(2)	3.170 (4)	Sn–C(3)	3.08 (2)	Al–Cl(2)	2.145 (6)	C(3)–C(4)	1.49 (3)
Sn–Cl(5)	2.614 (4)	Sn–C(4)	3.30 (2)	Al–Cl(3)	2.077 (6)	C(4)–C(5)	1.48 (3)
Sn–Cl(5$^{\mathrm{VI}}$)	2.659 (4)	Sn–C(5)	3.39 (2)	Al–Cl(4)	2.104 (7)	C(5)–C(6)	1.38 (3)
Sn–Cl(4$^{\mathrm{VII}}$)	3.324 (5)	Sn–C(6)	3.28 (2)	C(1)–C(2)	1.41 (3)	Sn–(COR)[d]	2.90 (2)
Sn–C(1)	3.11 (2)			C(1)–C(6)	1.37 (3)		
Selected Nonbonded Distances Less Than 4 A							
Cl(1)–C(2$^{\mathrm{VI}}$)	3.68 (2)	Cl(2)–C(5$^{\mathrm{VIII}}$)	3.88 (2)	Cl(3)–C(3$^{\mathrm{XI}}$)	3.73 (2)	Cl(5)–C(4$^{\mathrm{VIII}}$)	3.73 (2)
Cl(1)–C(3$^{\mathrm{VI}}$)	3.80 (2)	Cl(2)–C(5$^{\mathrm{IX}}$)	3.88 (2)	Cl(3)–C(5$^{\mathrm{IX}}$)	3.88 (2)	Cl(5)–C(1)	3.83 (2)
Cl(2)–C(4$^{\mathrm{VIII}}$)	3.70 (2)	Cl(2)–C(1)	3.89 (2)	Cl(3)–C(6$^{\mathrm{XII}}$)	3.94 (2)	Cl(5)–C(3$^{\mathrm{VI}}$)	3.89 (2)
Cl(2)–C(6)	3.76 (2)	Cl(3)–C(2$^{\mathrm{X}}$)	3.72 (2)	Cl(5)–C(2)	3.59 (2)		
Angles							
Sn–Cl(5)–Sn$^{\mathrm{VI}}$	99.7 (1)	Cl(5$^{\mathrm{I}}$)–Sn–Cl(1)	86.4 (1)	C(5)–C(4)–C(3)	116.1 (2)	Cl(3)–Al–Cl(1)	110.6 (3)
Cl(5)–Sn–Cl(5$^{\mathrm{VI}}$)	80.3 (1)	Cl(1)–Sn–Cl(4)	73.6 (1)	C(4)–C(5)–C(6)	124.0 (2)	Cl(4)–Al–Cl(2)	111.2 (3)
Cl(1)–Sn–Cl(2)	68.4 (1)	C(6)–C(1)–C(2)	124.9 (2)	C(1)–C(6)–C(5)	115.9 (2)	Cl(4)–Al–Cl(1)	109.3 (3)
Cl(5)–Sn–Cl(1)	83.5 (1)	C(3)–C(2)–C(1)	118.0 (2)	Cl(1)–Sn–(COR)[d]	152.1 (7)	Cl(2)–Al–Cl(1)	102.9 (3)
Cl(5)–Sn–Cl(2)	79.9 (1)	C(2)–C(3)–C(4)	120.8 (2)	Cl(3)–Al–Cl(4)	111.1 (3)		
Cl(5)–Sn–Cl(4$^{\mathrm{VII}}$)	146.6 (1)			Cl(3)–Al–Cl(2)	111.5 (3)		

[a] Esd's are given in parentheses. [b] Symmetry transformations: (I) $^1/_2 - x$, $^1/_2 - y$, $^1/_2 - z$; (II) $\bar{x}$, y, $^1/_2 - z$; (III) $^1/_2 - x$, $^1/_2 + y$, $\bar{z}$; (IV) $^1/_2 + x$, $^1/_2 + y$, $^1/_2 + z$; (V) x, $\bar{y}$, $^1/_2 + z$; (VI) $\bar{x}$, $\bar{y}$, $\bar{z}$; (VII) cell translation in $+z$; (VIII) cell translation in $-z$; (IX) $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$; (X) cell translation in $+y$; (XI) cell translation in $+y$ and $-z$; (XII) symmetry IX plus VIII. [c] COR = center of ring. [d] COR at $x = 0.1874$, $y = -0.1036$, $z = 0.2598$.

angles and their errors[23] were computed using the parameters and variance–covariance matrix from the last cycle of least-squares and are listed in Table IIa. The least-squares planes and deviations from the planes[24] are listed in Table IIIa.

$C_6H_6ClSn(AlCl_4)$, II. The structure was solved by standard heavy-atom methods as above. The structure converged to a final R and weighted R[17] of 0.070 and 0.090, respectively, with 118 parameters. All other quantities are as for I. Final atomic positional and temperature factors are in Table Ib. Interatomic distances, angles, and errors are in Table IIb. Other computed data are in Table IIIb.

Description and Discussion of Structures

Although the two crystal structures are not isomorphous, they have many common features and could be considered approximately isostructural. Each formally contains a planar $Sn_2Cl_2^{2+}$ unit whose center is a crystallographic center of symmetry (Figure 1). Each Sn^{2+} is then chelated by two chlorine atoms of an $AlCl_4^-$ species and in addition is bound to one chlorine of another $AlCl_4^-$ to generate an overall chain structure propagating in both cases in the [001] direction. This infinite chain is made up of alternating four-membered $Sn_2Cl_2^{2+}$ rings and eight-membered rings composed of two Sn^{2+} atoms from $Sn_2Cl_2^{2+}$ units and two bridging $AlCl_4^-$ species (Figure 2). The coordination polyhedron of Sn^{2+} is then completed by a slightly asymmetric π interaction with the aromatic moieties (Figure 1). If the center of the aromatic ring is considered as defining one coordination site, the coordination geometry about Sn^{2+} becomes a distorted octahedron (Figure 1 and Table II). The slightly asymmetric π interaction (see Sn–C distances, Table II) appears to arise via intermolecular nonbonding interactions between adjacent $Sn_2Cl_2^{2+}$ bridging chlorines and the aromatic moieties and is not an intrinsic electronic effect between Sn^{2+} and the aromatic.

Although the $Sn_2Cl_2^{2+}$ moiety is demanded to be planar by its center sitting on a crystallographic center of symmetry, it is not demanded that it be a regular square. It is, in fact, rectangular and the Sn–Cl distances of 2.616 (3) and 2.684 (3) Å for I and 2.614 (4) and 2.659 (4) Å for II specify this

Table III. Equations of Least-Squares Planes of the Type[a] $Ax + By + Cz - D = 0$

(a) p-$(CH_3)_2C_6H_4ClSn(AlCl_4)$			
$A = -0.1355, B = 0.8653, C = -0.4825, D = 3.3419$			
Deviations of Atoms from the Least-Squares Plane (Å)			
Cl(1)	0.108 (3)	Cl(3)	0.069 (3)
$Cl(1^{I})$[b]	−0.109 (3)	$Cl(2^{II})$	−0.068 (3)
Deviations of Atoms Not Included in the Least-Squares Plane (Å)			
Sn	−0.6567 (6)	Cl(5)	2.162 (3)
p-Xylene Plane			
$A = -0.2272, B = -0.8162, C = -0.5312, D = -6.2232$			
Deviations of Atoms from the Least-Squares Plane (Å)			
C(1)	0.01 (1)	C(5)	−0.02 (1)
C(2)	−0.00 (1)	C(6)	0.01 (1)
C(3)	−0.01 (1)	C(7)	−0.00 (1)
C(4)	−0.02 (1)	C(8)	0.02 (1)
(b) $C_6H_6ClSn(AlCl_4)$			
$A = -0.5753, B = 0.6044, C = -0.4770, D = -0.0001$			
Deviations of Atoms from the Least-Squares Plane (Å)			
Cl(2)	−0.002 (4)	Cl(5)	0.003 (4)
$Cl(4^{VII})$	0.002 (6)	$Cl(5^{VI})$	−0.003 (4)
Deviations of Atoms Not Included in the Least-Squares Plane (Å)			
Sn	−0.701 (5)	Cl(1)	2.132 (5)
Benzene Ring Plane			
$A = -0.5894, B = 0.7389, C = -0.3267, D = 3.3943$			
Deviations of Atoms from the Least-Squares Plane (Å)			
C(1)	−0.004	C(4)	−0.001
C(2)	−0.026	C(5)	−0.028
C(3)	0.029	C(6)	0.030

[a] x, y, and z refer to an internal orthogonal coordinate system. [b] Symmetry transformations: (I) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$; (II) $\bar{x}, y, \frac{1}{2} - z$; (VI) $-x, -y, -z$; (VII) cell translation in $+z$.

distortion. The remainder of the Sn–Cl distances are 3.208 (3), 3.214 (4), and 2.921 (3) Å for I and 3.170 (4), 3.324 (5), and 2.837 (4) Å for II. The sum of the tetrahedral radius of Sn and Cl is ~2.5 Å,[25] but since the present structures involve Sn^{2+}, better comparisons would be with the shortest Sn–Cl distance of 2.66 Å found in anhydrous stannous chloride,[26] with the 2.59-Å distance in $SnCl_2 \cdot 2H_2O$,[27] and with the 2.54- and 2.63-Å distances in the $SnCl_3^-$ ion.[28] On this basis the $Sn_2Cl_2^{2+}$ should be viewed as made up of Sn–Cl single bonds which are much stronger than the other Sn–Cl bonds in the remainder of the structure. The Sn–Cl bonds in π-$C_6H_6Sn(AlCl_4)_2$,[2b] on the other hand, were found to vary between 2.766 (2) and 3.280 (2) Å with the shortest distance being the axial Sn–Cl bond of a pentagonal-bipyramidal structure. The equatorial Sn–Cl bonds in that case were 3.280 (2), 3.020 (2), 2.907 (2), and 2.881 (2) Å. In the present two structures the equatorial plane in I is described by Cl(1), $Cl(1^{I})$, $Cl(2^{II})$, and Cl(3) (see least-squares planes, Table IIIa) with nonbridging Sn–Cl distances of 3.208 (3) and 3.214 (3) Å and in II the same plane is described by Cl(5), $Cl(5^{VI})$, Cl(2), and $Cl(4^{VII})$ with nonbridging Sn–Cl distances of 3.170 (4) and 3.324 (5) Å, respectively. Therefore, the nonbridging equatorial Sn–Cl distances in the present structure can be described as in π-$C_6H_6Sn(AlCl_4)_2$ as one-electron bonds (particularly since in π-$C_6H_6Sn(AlCl_4)_2$ a simple MO description fits such a picture quite well). In π-$C_6H_6Sn(AlCl_4)_2$ the Sn is displaced out of the equatorial plane 0.591 (1) Å toward the aromatic moiety and here (Table III) in I Sn is displaced by 0.657 (1) Å and in II by 0.701 (1) Å. As before, this displacement can be most readily understood in terms of nonbonding interactions between the equatorial chlorine atoms and the aromatic moiety. The Sn–C(aromatic) distances vary from 2.93 (1) to 3.27 (1) Å in I and from 3.05 (2) to 3.39 (2) Å in II compared to 3.05 (1) Å for all Sn–C distances (within experimental error) for π-$C_6H_6Sn(AlCl_4)_2$. As was indicated above, we feel that the variation in Sn–C distances in I and II is primarily due to intermolecular nonbonding interactions rather than any electronic effects between Sn^{2+} and aromatic. The C–C and Al–Cl distances and angles seem to be normal for this type of compound.

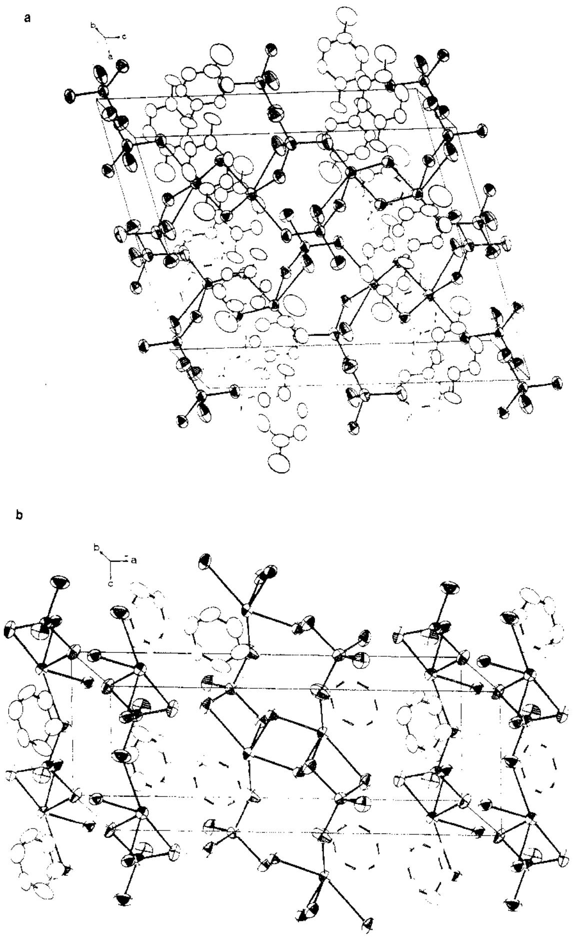

Figure 2. (a) ORTEP[31] diagram of the contents of the unit cell of p-$(CH_3)_2C_6H_4ClSn(AlCl_4)$. The origin of the unit cell is at the upper left hand corner displaced toward the center. The observer is looking in the direction of positive b from this origin. The carbon atoms are denoted by open circles for reasons of simplicity. The ellipsoids are drawn at the 50% probability level. ORTEP[31] diagram of the contents of the unit cell of $C_6H_6ClSn(AlCl_4)$. The origin of the unit is again displaced toward the center from the upper left hand corner and the viewer is looking toward positive b. However, in this case negative a goes across left to right at the top. All else is as in (a).

It seems clear from the above description that the Sn–Cl bonds in $Sn_2Cl_2^{2+}$ may be regarded as normal Sn–Cl single bonds, whereas the other Sn–Cl bonds are very similar to those found in π-$C_6H_6Sn(AlCl_4)_2$ in which the equatorial bonds are ~$^1/_2$ electron-pair bonds and the axial Sn–Cl approaches a single electron-pair Sn–Cl bond. In addition, the tin–aromatic interaction must be quite similar in I, II, and π-$C_6H_6Sn(AlCl_4)_2$, i.e., primarily (in the simplest sense) a donor–acceptor interaction between the highest filled aromatic molecular orbitals and the lowest empty (5p) orbitals of Sn oriented in the equatorial plane. For a detailed discussion of this bonding, see ref 2b.

It is interesting to note that the phase diagram of $SnCl_2 \cdot AlCl_3$[29] indicates a compound of composition $SnCl(AlCl_4)$; i.e., it suggests the dimer $Sn_2Cl_2^{2+}$ found in I and II. Furthermore, whereas the analogous $PbCl(AlCl_4)$ is not known and since we have not been able to make π-$ArClPb(AlCl_4)$, we have made π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$ and determined its structure,[30] which is similar to that of π-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$.[2b]

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Registry No. I, 36345-35-4; II, 36222-97-6.

Supplementary Material Available: Observed and calculated structure factors together with unobserved structure factors (26 pages). Ordering information is given on any current masthead page.

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(13) A single general reflection of average intensity in the middle of the λ, ϕ, 2θ range used for data collection has been found by us to be as reliable as several standards, particularly if they are well chosen (at least for small-molecule structures). With modernization of the instrument and subsequent faster driving speeds this philosophy has been replaced by that of multiple standard peaks (measurements). In addition, for these structures reported herein, three independent general reflections were measured once a day and their decomposition paralleled that of the single standard.
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Synthesis and Structure of the $B_{11}H_9Se_3^{2-}$ Ion

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Reaction of $NaB_{11}H_{14}(dioxane)_{2.5}$ with ammonium polyselenide formed the $B_{11}H_9Se_3^{2-}$ ion in low yield. The structure of this unexpected product has been determined by X-ray diffraction techniques. The dianion is a disubstituted derivative of $B_{11}H_{11}^{2-}$. The Se_3 chain is bonded to two adjacent boron atoms of the closo cage and is exo to the polyhedral boron structure. Boron-11 NMR suggests that the molecular ion is fluxional at room temperature.

Recently we have found that sodium polyselenide is a useful reagent for insertion of one or two selenium atoms into cage borane structures. For example, reaction of decaborane(14) with $Na_2(Se_x)$ formed $B_{10}H_{11}Se^{-1}$ and treatment of $Na(B_9H_{14})$ with this reagent gave $B_9H_9Se_2$.[2] We thought that reaction of the $B_{11}H_{14}^-$ ion with polyselenide ion would lead to the known molecule $B_{11}H_{11}Se$.[3] However, the product of this reaction was a red dianion. The synthesis and X-ray structure elucidation of this novel molecular ion are presented in this report.

Experimental Section

The boron-11 NMR spectrum was obtained at 70.6 MHz with a Varian HR-220 spectrometer and was externally referenced to $BF_3 \cdot O(C_2H_5)_2$ (with positive values downfield). The infrared spectrum was obtained as a KBr disk employing a Perkin-Elmer 283 spectrometer. The ultraviolet–visible spectrum was measured with a Cary 14 instrument. The elemental analysis was performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

The $NaB_{11}H_{14}(dioxane)_{2.5}$ was prepared by the literature procedure.[4]

$[(C_2H_5)_4N]_2B_{11}H_9Se_3$. The ammonium polyselenide solution was prepared as previously described employing sodium (0.64 g, 0.028 mol) and selenium (4.2 g, 0.053 g-atom).[1] A solution of $NaB_{11}H_{14}(dioxane)_{2.5}$ (5.0 g, 0.013 mol) in 5 mL of water was added to the polyselenide solution, and the reaction mixture was stirred for 48 h at room temperature. After this time, a saturated solution of tetraethylammonium chloride was added to the mixture until precipitation was complete. The resulting solid was isolated by filtration in air and was washed with two 10-mL portions of water. The crude solid was dissolved in a minimum of acetonitrile. A few milliliters of water was added to the solution, and then the solvent was slowly removed by rotary evaporation to give 0.54 g (6% yield based on $NaB_{11}H_{14}(dioxane)_{2.5}$) of $[(C_2H_5)_4N]_2B_{11}H_9Se_3$ as orange plates.

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