Heteroatom Chemistry
Volume 1, Number 2, 1990

π-Complexes of p-Block Elements: (η^6-Mesitylene)tin(II) Chloride Tetrachloroaluminate(III), a Coordination Polymer

Hubert Schmidbaur,* Thomas Probst, Oliver Steigelmann, and Gerhard Müller

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-8046 Garching, Federal Republic of Germany

Received 14 June 1989.

ABSTRACT

(η^6-1,3,5-Trimethylbenzene)tin(II) chloride tetrachloroaluminate(III), (η^6-1,3,5-$C_6H_3Me_3$)SnCl ($AlCl_4$), has been obtained from the reaction of anhydrous $SnCl_2$ and $AlCl_3$ in the molar ratio 1 : 2 in excess mesitylene as a solvent. The compound crystallizes in monoclinic needles, space group $P2_1/n$, containing a coordination polymer with planar four-membered rings Sn-Cl-Sn-Cl as the fundamental structural units. Each tin(II) atom of these rings is η^6-bonded to a mesitylene ring, with the metal approximately centered over the aromatic hydrocarbon at a distance of 2.71 Å. Each of the tin(II) atoms is further connected to two tetrachloroaluminate counter ions, one of these monodentate and one bidentate. Through this mono/bidentate contacts a one-dimensional coordination polymer is generated with crystallographic centers of inversion in the middle of the $Sn(Cl)_2Sn$ and $Sn(AlCl_4)_2Sn$ rings. The structure is similar to that of the analogous benzene complex, but not identical owing to a different connectivity pattern. Also, the arene-Sn(II) distance is much shorter in the mesitylene complex (2.71 Å) than in the benzene complex (2.90 Å), indicating that the trimethylbenzene molecule is a much better donor than benzene.

INTRODUCTION

In contrast to the chemistry of complexes of the d-block elements ("transition elements") with aromatic hydrocarbons, the coordination of neutral arenes to p-block elements (a part of the "main group elements") for a long time has received only limited attention. Apart from some earlier studies, it has been only recently that major contributions could also be made to this neglected field [1–6]. After a series of very successful studies with the heavier, low-valent metals of Group 13 (Ga, In, T1 [1, 2]) and Group 15 (As, Sb, Bi [5, 6]), the congeners in Group 14 have also become the subject of current investigation. Already in the early 1970s it has been discovered that both tin(II) and lead(II) form complexes of 1 : 1 stoichiometry with benzene and *p*-xylene. Though of relatively low stability, several compounds could be isolated and positively identified. Among those the four species $(C_6H_6)SnCl-(AlCl_4)$ [3], $(p-C_6H_4Me_2)SnCl(AlCl_4)$ [3], and $(C_6H_6)M-(AlCl_4)_2 \cdot C_6H_6$ (M = Sn [3], M = Pb [4]) have been structurally characterized. In each case the M(II) metal is centered above one arene ligand (hexahapto coordination η^6). A similar situation was also found in tin(II) diphenyldithiophosphate, where the phenyl groups of the anions clearly show coordination to the tin(II) centers [3b]. In a detailed study of the benzene/$SnCl(AlCl_4)$ system a new phase was recently discovered in which *two* benzene molecules are coordinated to the tin(II) center. This 2 : 1 phase, $(C_6H_6)_2Sn-Cl(AlCl_4)$, contains bent sandwich units $(C_6H_6)_2Sn^{2+}$ bridged by Cl^- and $AlCl_4^-$ anions to give centrosymmetrical dimers [7], while another 1 : 1 phase, with hexamethylbenzene as the arene ligand, $(C_6Me_6)SnCl-(AlCl_4)$, forms centrosymmetrical tetramers [8]. In an attempt to develop fur-

---

* To whom correspondence should be addressed.

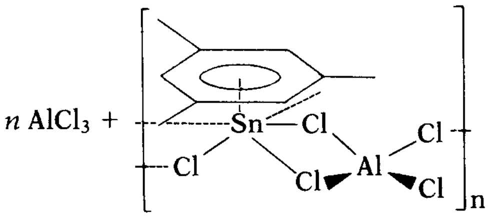
1042-7163/90/$3.50 + .25

ther the systematics of arene complexes of Group 14 metals, we have now also studied the related mesitylene system. With benzene, *p*-xylene, and hexamethylbenzene already well represented, it was hoped that the mesitylene example would confirm the evidence for regularities in complex stability and geometrical features obtained in the previous results.

Preparation and Properties of *($1,3,5$-$C_6H_3Me_3$)$SnCl(AlCl_4)$*

For the synthesis of the title complex anhydrous tin(II) dichloride and aluminum trichloride in the molar ratio 1 : 2 were mixed in dry mesitylene and heated under reflux until all solids had dissolved. During slow cooling of the resulting clear colorless solution, crystals of a product separated that were shown to consist of the 1 : 1 complex of mesitylene and $SnCl(AlCl_4)$. Thus one $AlCl_3$ equivalent was not integrated into the complex and remained in solution. Nevertheless, its presence was found to be essential for a ready formation of the product. Smaller amounts of $AlCl_3$ lead to slower and incomplete reaction. Though sensitive to moist air, the complex shows good thermal stability (m.p. 160–161°C).

n 1,3,5-$C_6H_3Me_3$ + n $Sn(AlCl_4)_2 \rightarrow$



The compound, which was shown to be a coordination polymer (see above), cannot be redissolved in pure mesitylene. Attempts of recrystallization lead to decomposition.

Description and Discussion of the Crystal Structure of *(η^6-$C_6H_3Me_3$)$SnCl(AlCl_4)$*

The crystals of the title compound are monoclinic, space group $P2_1/n$, with dimensional details as listed in Table 1. The structure features a one-dimensional coordination polymer shown in Figure 1. Pairs of Sn^{2+} cations are bridged by pairs of Cl^- anions to form a four-membered ring $Sn_2Cl_2^{2+}$ centered around a crystallographical center of inversion. Each of the equivalent tin(II) atoms is η^6-coordinated to one mesitylene molecule with a distance of 2.71 Å between the metal and the center of the arene plane. Each tin(II) atom is further coordinated to two $AlCl_4^-$ counterions, one of which is a chelating bidentate, while the other is only a monodentate ligand for the tin atom under consideration. Related by symmetry, these two anions have the inverted ligand functionality (mono-/bidentate) relative to another tin(II) center which is part of a neighboring $Sn_2Cl_2^{2-}$ unit.

TABLE 1 Crystal Data and Structure Solution

Formula	$C_9H_{12}AlCl_5Sn$
M_r	443.133
Space group	$P2_1/n$ (No. 14)
a (Å)	9.293 (1)
b (Å)	12.654 (1)
c (Å)	13.770 (1)
β (°)	95.78 (1)
V (Å³)	1611.0
Z	4
ρ_{calc} (g cm^{-3})	1.827
μ (MoK_α) (cm^{-1})	24.6
T (°C)	−50
$(\sin \vartheta/\lambda)_{max}$ (Å^{-1})	0.639
hkl range	+11, +15, ±17
Number of measured refl.	3879
Number of unique refl.	3503
Number of observed refl.	3131
Number of refined parameters	145
R^a	0.028
$R_w{}^b$	0.031
$\Delta\rho_{fin}$(e/Å³)	+0.59/−0.65

[a] $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$;
[b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma wF_0^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_0)$

Assigning one coordination site to the arene, the coordination number of the tin centers is thus 6, and the coordination geometry is strongly distorted octahedral. The Sn-Cl distances range from 2.667(1) to 3.195(1) Å, with the shortest values for the edges of the four-membered ring $Sn_2Cl_2^{2+}$ (Sn-$Cl_{1/1'}$) and the longer ones for the tin contacts with the $AlCl_4^-$ groups. Except for the angles Cl1-Sn-Cl2 (86.4(1)°) and Cl1′-Sn-Cl2 (88.8(1)°), all angles between cis-coordinated atoms at the tin center deviate strongly from 90°.

The normal to the arene plane and the line connecting the tin atom and the center of the six-membered ring of the mesitylene form an angle of only 6.7°, which is a good indicator for η^6-hapticity.

The tetrahedral environment of the aluminum atoms is quite regular with only small deviations from standard dimensions. The Al-Cl distances are within the narrow limit 2.106(1)–2.173(1) Å. The shortest of these relates to the only terminal, non-coordinating chlorine atom Cl5. A list of selected bond distances and angles is presented in Table 2, and atomic coordinates and thermal displacement parameters are listed in Table 3.

The most important result regarding the structural details of the title compound is the short Sn-to-ring distance. At 2.71 Å, the mesitylene ring is closer to the metal not only than the benzene ring

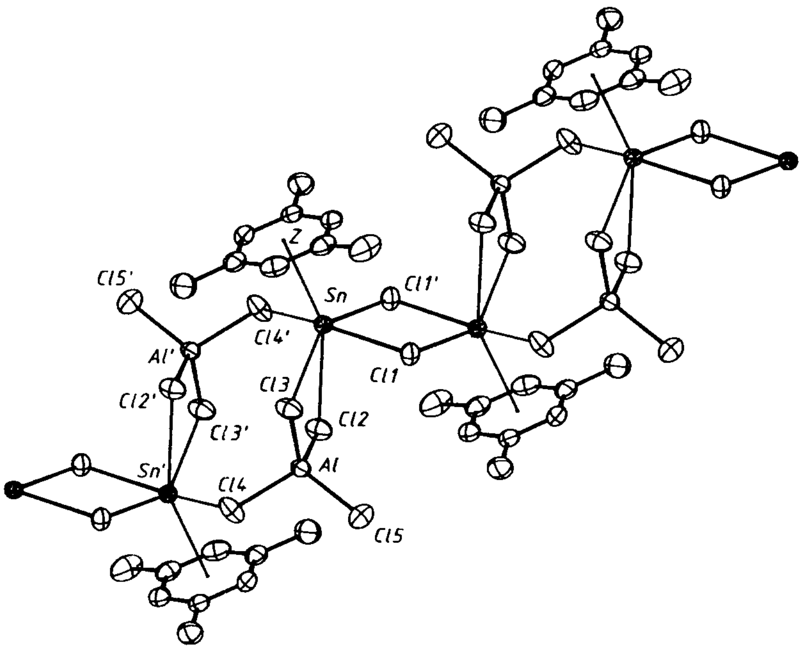


FIGURE 1 Crystal structure of the $[\eta^6\text{-}(1,3,5\text{-}C_6H_3Me_3)Sn\text{-}Cl(AlCl_4)]$ coordination polymer (ORTEP, 50% probability ellipsoids).

(2.90 Å), but also than the *p*-xylene ring (2.77 Å) in the analogous compounds [3a–c]. It is only the hexamethylbenzene molecule that is still more tightly bonded to Sn(II) (at 2.60/2.73 Å, two different sites), in agreement with predictions based on the concept that the arenes function mainly as donors to the metal in these complexes.

The benzene and the *p*-xylene complex of $SnCl(AlCl_4)$ have related structures [3a,b]. They differ from the present mesitylene complex in that the connectivity at the tin(II) centers follows another pattern: In the mesitylene complex the mono- and bidentate $AlCl_4^-$ contacts are found in what one can specify as a facial (or cis) combination at the (distorted !) octahedron, while in the previous compounds they are closer to meridional (or trans). This leads to a chain-like coordination polymer for the mesitylene compound, with alternating $SnCl_2Sn$ and $Sn(AlCl_4)_2Sn$ units and the tin atoms as the spiro centers (Figure 1), whereas double strings of tin atoms are present in the benzene and *p*-xylene analogues [3a,b]. In the latter (C_6H_6,

TABLE 2 Selected Bond Distances (Å) and Angles (°) with standard deviations in parentheses.

Sn-Cl1	2.667(1)	Sn-Cl1′	2.646(1)
Sn-Cl2	2.990(1)	Sn-Cl3	3.193(1)
Sn-Cl4′	3.195(1)		
Sn-Z	2.71		
Al-Cl2	2.173(1)	Al-Cl3	2.134(1)
Al-Cl4	2.127(1)	Al-Cl5	2.106(1)
Cl1-Sn-Cl1′	79.3(1)	Sn-Cl1-Sn′	100.7(1)
Cl1-Sn-Cl2	86.4(1)	Cl1′-Sn-Cl2	88.8(1)
Cl1-Sn-Cl3	75.3(1)	Cl1′-Sn-Cl3	146.0(1)
Cl1-Sn-Cl4	148.0(1)	Cl1′-Sn-Cl4	73.6(1)
Cl2-Sn-Cl3	67.6(1)	Cl2-Sn-Cl4	76.6(1)
Cl3-Sn-Cl4	120.7(1)		
Cl2-Al-Cl3	106.1(1)	Cl2-Al-Cl4	109.3(1)
Cl2-Al-Cl5	109.5(1)	Cl3-Al-Cl4	109.5(1)
Cl3-Al-Cl5	112.0(1)	Cl4-Al-Cl5	110.4(1)

TABLE 3 Atomic Coordinates and Thermal Displacement Parameters

Atom	*X/A*	*Y/B*	*Z/C*	*U(eq.)*
Sn	0.18492(2)	0.08489(1)	0.03656(1)	0.035
Al	0.38165(9)	0.02717(7)	−0.19129(6)	0.038
Cl_1	−0.03075(8)	0.06845(6)	−0.10585(5)	0.038
Cl_2	0.33802(9)	−0.07750(6)	−0.07261(6)	0.054
Cl_3	0.31256(9)	0.18063(6)	−0.15145(6)	0.060
Cl_4	0.60795(8)	0.02940(7)	−0.20381(6)	0.066
Cl_5	0.2683(1)	−0.02624(8)	−0.32221(6)	0.062
C_{10}	0.3064(4)	0.3032(2)	0.1268(2)	0.048
C_{11}	0.2825(4)	0.2409(2)	0.2060(2)	0.044
C_{12}	0.1446(3)	0.2029(2)	0.2198(2)	0.041
C_{13}	0.0291(3)	0.2285(2)	0.1504(2)	0.050
C_{14}	0.0494(4)	0.2942(2)	0.0707(2)	0.057
C_{15}	0.1887(4)	0.3292(3)	0.0597(2)	0.056
C_{101}	0.4566(5)	0.3416(3)	0.1123(3)	0.073
C_{121}	0.1196(4)	0.1375(3)	0.3079(2)	0.055
C_{141}	−0.0776(5)	0.3271(3)	0.0007(3)	0.090

p-$C_6H_4Me_2$), a given tin atom is linked to two other tin atoms of two different neighboring Sn_2Cl_2 units through $AlCl_4$ bridges, while in the former (1,3,5-$C_6H_3Me_3$) a given tin atom is linked to one and the same tin atom of the neighboring Sn_2Cl_2 unit through both $AlCl_4$ bridges (Figure 2, **A** and **B**). It is plausible that these differences are due to steric effects. The bulkier (and more tightly bonded) mesitylene molecule is more easily accommodated at the single-stranded structure as compared to the double-stranded structure found for the coordination polymers with benzene or *p*-xylene.

EXPERIMENTAL

General

The experiments were carried out in an atmosphere of dry, purified nitrogen. Mesitylene was dried over sodium/potassium alloy and distilled under nitrogen. Glassware was oven-dried and filled with nitrogen. Anhydrous $SnCl_2$ was commercial grade, and $AlCl_3$ was freshly sublimed.

Polymeric (η^6-1,3,5-trimethylbenzene)tin(II) Chloride Tetrachloroaluminate

Anhydrous tin(II) dichloride (0.76 g, 4.01 mmol) and anhydrous aluminum trichloride (1.10 g, 8.25 mmol) were added to 200 mL of 1,3,5-trimethylbenzene at room temperature, and the mixture was heated under reflux for 20 min until the reagents had dissolved. The mixture was allowed to cool slowly (over a period of 8 h) to room temperature. Colorless crystals were formed. The mother liquor was decanted and the product collected; yield 1.93 g (93%), m.p. 160–161°C. The product decomposes in air with rapid hydrolysis. It cannot be recrystallized from pure mesitylene, benzene, toluene, or mixtures of these.

Crystal Structure Determination

A suitable single crystal was sealed into a glass capillary under an argon atmosphere. According to diffractometer measurements (Syntex $P2_1$) the

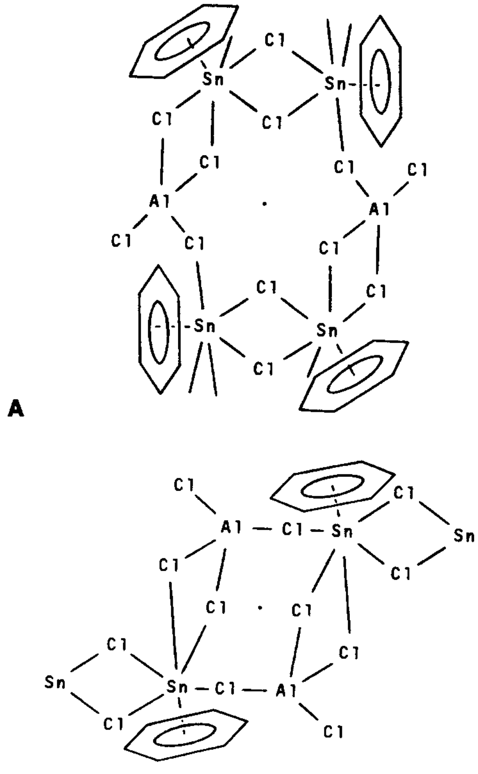


FIGURE 2

sample crystallizes in the monoclinic space group $P2_1/n$. Reduced cell calculations did not reveal any higher symmetry. Pertinent data are summarized in Table 1. The integrated intensities of the reflections were measured on a four-cycle diffractometer (MoK_α radiation, graphite monochromator) and corrected for Lp- and absorption effects (rel. transmission 0.71–1.00). The structure was solved by Patterson methods (SHELXS-86, MS-DOS version) and completed by difference Fourier syntheses. After refinement of all nonhydrogen atoms with anisotropic displacement parameters, ten hydrogen atoms could be located in a difference Fourier map, two were calculated at idealized geometrical positions. In the final refinement cycles hydrogen atoms were included with fixed atom contributions ($U_{iso} = 0.05$ Å^2).

The fractional atomic coordinates and isotropic displacement parameters are listed in Table 3. Additional data have been deposited at Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen. (Requests should be accompanied by the depository number CSD-54330, the names of the authors and the full literature quotation.)

Acknowledgment

Generous support of this work by Deutsche Forschungsgemeinschaft (Leibniz-Programm) and by Fonds der Chemischen Industrie is gratefully acknowledged. J. Riede is thanked for carefully setting up the X-ray data set.

References

[1] H. Schmidbaur, *Angew. Chem.*, *97*, 1985, 893; *Angew. Chem., Int. Ed. Engl.*, *24*, 1985, 893 (review).

[2] H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Organometallics*, *5*, 1986, 1647; H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Z. Naturforsch. B, Chem. Sci.*, *42*, 1987, 147; M. Uson-Finkenzeller, W. Bublak, B. Huber, G. Müller, *Z. Naturforsch. B, Chem. Sci.*, *41*, 1986, 346; J. Beck, J. Strähle, *Z. Naturforsch. B, Chem. Sci.*, *41*, 1986, 1381; H. Schmidbaur, R. Nowak, B. Huber, G. Müller, *Z. Naturforsch. B, Chem. Sci.*, *43*, 1988, 1447; S. H. Strausz, M. D. Noirot, O. P. Anderson, *Inorg. Chem.*, *25*, 1986, 3850; H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Helv. Chim. Acta*, *69*, 1986, 1742.

[3] [a] M. S. Weininger, P. F. Rodesiler, A. G. Gash, E. L. Amma, *J. Am. Chem. Soc.*, *94*, 1972, 2135; [b] M. S. Weininger, P. F. Rodesiler, E. L. Amma, *Inorg. Chem.*, *18*, 1979, 751; [c] P. F. Rodesiler, T. Auel, E. L. Amma, *J. Am. Chem. Soc.*, *97*, 1975, 7405; [d] J. L. Lefferts, M. B. Hossain, K. C. Molloy, D. van der Helm, J. J. Zuckerman, *Angew. Chem.*, *92*, 1980, 326; *Angew. Chem., Int. Ed. Engl.*, *19*, 1980, 306.

[4] A. G. Gash, P. F. Rodesiler, E. L. *Amma*, *Inorg. Chem.*, *13*, 1974, 2429.

[5] B. N. Menshutkin, *Zh. Russ. Fiz. Khim. Ova*, *43*, 1911, 1298; W. Smith, G. W. Davis, *J. Chem. Soc.*, *41*, 1882, 411; D. Mootz, V. Händler, *Z. Anorg. Allg. Chem.*, *533*, 1986, 23, and references therein; W. Frank, J. Weber, E. Fuchs, *Angew. Chem.*, *99*, 1987, 68; Angew. Chem., Int. Ed. Engl., 26, *1987, 74.*

[6] H. Schmidbaur, W. Bublak, B. Huber, G. Müller, *Angew. Chem.*, *99*, 1987, 248; *Angew. Chem., Int. Ed. Engl.*, *26*, 1987, 234; H. Schmidbaur, J. M. Wallis, R. Nowak, B. Huber, G. Müller, *Chem. Ber.*, *120*, 1987, 1837; H. Schmidbaur, R. Nowak, A. Schier, J. M. Wallis, B. Huber, G. Müller, *Chem. Ber.*, *120*, 1987, 1829; H. Schmidbaur, R. Nowak, B. Huber, G. Müller, *Organometallics*, *6*, 1987, 2266; A. Schier, J. M. Wallis, G. Müller, H. Schmidbaur, *Angew. Chem.*, *98*, 1986, 742; *Angew. Chem., Int. Ed. Engl.*, *26*, 1986, 725.

[7] H. Schmidbaur, T. Probst, B. Huber, O. Steigelmann, G. Müller, *Organometallics* (in press).

[8] H. Schmidbaur, T. Probst, B. Huber, G. Müller, C. Krüger, *J. Organometal. Chem.*, *365*, 1989, 53.