Heavy-Metal π Complexes, 12[◇]

A Monomeric Bis(arene)lead(II) Complex with a Plumbocene-Like Bent Sandwich Structural Unit – Structure of $[Pb(1,2\text{-}C_6H_4Me_2)_2(AlCl_4)_2]$[☆]

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Bis(*o*-xylene)lead(II) bis(tetrachloroaluminate), obtained from lead(II) chloride and aluminium trichloride in *o*-xylene, has been shown by X-ray crystallography to be a mononuclear lead complex with point group symmetry C_2. The two aromatic ligands are arranged similarly to those in monomeric plumbocene. The coordination sphere is completed by two bidentate $AlCl_4^-$ ions. The lead center uses about a quarter of its bonding capability for each of the four ligands

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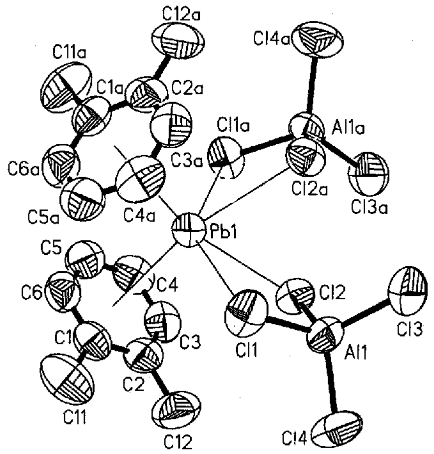
Since the pioneering work of Amma et al. dealing with the coordination polymeric $\{[(C_6H_6)Pb(AlCl_4)_2]\ C_6H_6\}_\infty$[1], very few other arene complexes of lead[2][3][4] have been reported. All the characterized compounds[1][4] are monoarene complexes of the half-sandwich type, with the arene rather weakly bonded and the anionic ligands more strongly bonded to the metal center. We now report on the synthesis and characterization of a monomeric bis(arene)lead(II) complex with an unexpectedly simple structure. The $(o\text{-xylene})_2Pb$ structural unit is related to the well-known structure of plumbocene[5][6][7] as well as to the $(arene)_2M$ units of dimeric bis(arene)gallium(I) and bis(arene)thallium(I) tetrachlorometallates.[8][9]

Highly purified $PbCl_2$ and $AlCl_3$ in the molar ratio of 1:2 was dissolved in absolutely dry *o*-xylene to give a clear yellow solution. From this solution a pale yellow compound, **1**, was crystallized. Absolute exclusion of moisture during the preparation process is very important, otherwise the compound is accompanied by adhesive yellow or orange oils. If present, these oils make the characterization of the compound very difficult. When enclosed in an ampoule with dry argon, **1** is fairly stable at room temperature in the absence of light, but loses all the coordinated arene moieties when heated up to 54°C. The result of an elemental analysis showed that it formally contains the three starting materials in a 1:2:2 ratio, compatible either with a compound similar to the benzene complex mentioned above, or with a bis(arene)lead complex of the formula $[Pb(C_8H_{10})_2(AlCl_4)_2]$.

According to the results of an X-ray structure determination, solid **1** consists of a monomeric complex with two arene ligands in a distorted η^6 mode of coordination and two bidentate $AlCl_4^-$ ligands at the central Pb^{2+} ion, that is, **1** has a completely different structure to the analogous benzene complex. **1** was shown to have C_2 symmetry. In contrast to all other reported group 14 metal complexes with monocyclic arenes, the anionic ligands in **1** do not function as bridging ligands building up a higher nuclear arrangement, and thus **1** may be considered to be an arene stabilized monomeric lead(II) bis(tetrachloroaluminate).

Figure 1. Diagram of **1** (displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity; symmetry operator: a: $-x$, y, $0.5-z$); selected bond lengths (Å) and angles (°): Pb(1)−Cl(1) [−Cl(2)] 2.9693(15) [3.0770(15)]; Pb(1)−C(1) [−C2, −C3, −C4, −C5, −C6] 3.309(5) [3.216(5), 3.083(6), 3.067(5), 3.176(6), 3.291(6)]; Al−Cl1 [−Cl2, −Cl3, −Cl4] 2.168(2) [2.166(2), 2.100(3), 2.097(2)]; Cl1−Al1−Cl2 [−Cl3, −Cl4] 101.5 [110.4, 111.7]; Cl2−Al1−Cl3 [−Cl4] 111.8 [109.3]; Cl3−Al1−Cl4 111.7; shortest distances to metal atoms of neigboring complexes are: Pb···Pb 8.861; Pb···Al 6.650 Å.



A closer inspection of the structure (Figure 1), shows that there is no significant structural difference between the arene ligands of **1** and free *o*-xylene molecules. Bond lengths and angles in the $AlCl_4^-$ ligands are as expected, taking into account the interaction with the lead center. All Pb−Cl distances (see legend to Figure 1) within **1** are longer than the shortest distance in solid lead(II) chloride[10] (2.87 Å). Therefore the interactions of the lead

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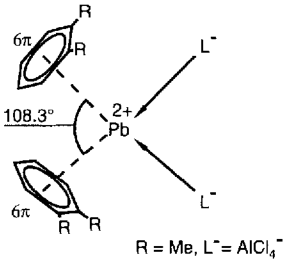
center with the tetrachloroaluminate ligands must be highly ionic, suggesting that **1** is a trio of arene-stabilized ions, rather than a molecule.

The ring-carbon to lead distances are in the range 3.067(5)−3.291(6) Å [Pb−ring center 2.874(3) Å] compared to 2.69(1)−2.90(1) Å in the solid state structure of decamethylplumbocene[7] [plumbocene[6] 5 × 2.778(16) Å]. The weaker bonding of the aromatic ligands in **1**, as well as the smaller ring center−Pb−ring center angle (108.3°; plumbocene 135°; decamethylplumbocene 151°), are easily explained by the coordination of the anionic ligands in the opposite half of the coordination sphere.



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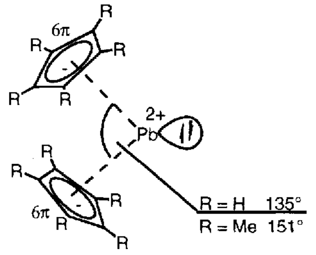

For the plumbocenes, an approximate Pb−Cp bond order of 1 must be assumed for each of the ligands, resulting in a valence sum of 2 for the lead(II) center.[11] An estimate of the Pb−Cl bond valencies based on the concept of Brown[12], using an r_0 value taken from the gas phase structure of lead(II) chloride[13], suggests that the lead atom of **1** uses about a quarter of its bonding capability for each of the four ligands.

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Experimental Section

General: Preparation and handling of the substance were performed using a modified Stock-type vacuum apparatus and P_4O_{10}-dried, deoxygenated nitrogen or argon as inert gas. − X-ray: Stoe IPDS. − DTA: Linseis DTA. − EA: Perkin−Elmer 240 Mikroanalyzer.

Bis(o-xylene)lead(II) Bis(tetrachloroaluminate) {$[Pb(1,2\text{-}C_6H_4Me_2)_2(AlCl_4)_2]$ (**1**)}: A mixture of $PbCl_2$ (380 mg, 1.37 mmol), that was kept at 200°C in vacuo for several days, and $AlCl_3$ (358 mg, 2.72 mmol), purified as described in Ref.[14], was dissolved in 5 mL of *o*-xylene, dried by refluxing in the presence of sodium metal, resulting in a yellow solution. Within hours, its color faded to pale yellow accompanied by the precipitation of some $PbCl_2$, which was filtered off. The filtrate was kept in the dark at 5°C, and after a week, pale yellow crystals of **1** (240 mg; 12% based on $AlCl_3$) were isolated. Elemental analysis: $C_{16}H_{20}Al_2Cl_8Pb$ (757.07 gmol^{-1}): calcd. C 25.38, H 2.66; found C 24.5, H 2.5.

DTA: According to the results of preliminary DTA measurements there are at least 3 endothermic effects in the temperature range 25−54°C, indicating either phase transformations or loss of arene. Above 54°C the sample is completely free of arene.

X-ray Crystal Structure Analysis of $C_{16}H_{20}Al_2Cl_8Pb$ (**1**): M_r = 757.07 g mol^{-1}, monoclinc space group $C2/c$, a = 17.266(3), b = 10.329(2), c = 15.060(3), β = 92.97(3)°, V = 2682.2(9) Å^3 , Z = 4, D_x = 1.875 g.cm^{-3}, μ = 7.155 mm ^{1} (λ = 0.71073 Å), T = 298 K, pale yellow crystal of dimensions 0.5 × 0.4 × 0.35 mm in a thin-walled glass capillary. 9257 reflection data were collected on a Stoe Imaging Plate Diffraction System. Face indexed numerical absorption[15] correction was applied ($T_{\min}$ = 0.0518; $T_{\max}$ = 0.1195). The structure was solved by the heavy atom method[16] and refined (132 parameters) by full matrix least squares calculations on F^2, using all but 15 of the most negative of 2050 unique reflections to final R_1 = 0.027 (all data), wR_2 = 0.067 (all data), $w = 1/[\sigma^2(F_o^2)+(0.0332P)^2+3.5279P]$ where $P = (F_o^2+2F_c^2)/3$, S = 1.116[17]. Largest peak and hole in the final difference map are 0.816 e/Å and −0.600 e/Å, respectively. Anisotropic displacement parameters were refined for all atoms heavier than hydrogen. Most of the hydrogen atoms could be located in a difference fourier map. In the final refinement cycles they were included in idealized positions, and the methyl groups were allowed to rotate around the C−C bond.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-100655. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.)+44(1223)336-033, e-mail: deposit@chemcrys.cam.ak.uk].

☆ Dedicated to Professor *C. G. Kreiter* on the occassion of his 60th birthday.

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[11] In the bond valence concept, the valence *V* of an atom is set as being equal to its oxidation number, so that it is an integer. *V* is assumed to be distributed over all the bonds between the central atom and the atoms of its environment, according to the valence sum rule $V = \Sigma s$, where *s* is the bond valence (bond order) of a particular bond. If we consider the Pb−Cp interaction as *one* bond, $V = 2s$(Pb−Cp) results for $PbCp_2$, i.e. s(Pb−Cp) = 0.5 *V*.
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