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Metal Ion-Aromatic Complexes. XV. Synthesis, Structure, and Bonding of π-$C_6H_6Pb(AlCl_4)_2{\cdot}C_6H_6$

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The synthesis of π-$C_6H_6Pb(AlCl_4)_2{\cdot}C_6H_6$ has been accomplished and its crystal structure determined. The local environment of the Pb(II) is that of a distorted pentagonal bipyramid (6Cl) with an axial coordination site occupied by the center of a benzene ring. The remaining benzene is a molecule of solvation far removed from the metal. The overall structure is described as a chain in which $AlCl_4^-$ tetrahedra are bridged together by Pb(II) and the other $AlCl_4^-$ behaves as a chelating ligand to form an axial and an equatorial Pb-Cl bond. The Pb-Cl distances vary from 2.854 (8) to 3.218 (9) Å. The average Pb-C (bound) distance is 3.11 (4) Å and the Pb-center of ring distance is 2.77 (4) Å. A qualitative molecular orbital model is presented and adequately accounts for many of the Pb(II) coordination features. The crystal data are: monoclinic $P2_1/n$, $a = 11.365$ (1) Å, $b = 17.307$ (2) Å, $c = 12.707$ (2) Å, $\beta = 110.14$ (1)°, λ 0.71068 Å; $\rho_o = 1.7$-2.0 g cm^{-3}, $\rho_c = 1.99$ g cm^{-3}, $Z = 4$, π-$C_6H_6Pb(AlCl_4)_2{\cdot}C_6H_6$, $\mu = 80.6$ cm^{-1}. The structure was determined from 2075 counter-measured intensity data at room temperature and refined by full matrix least squares including anomalous dispersion corrections for Pb, Cl, and Al, as well as anisotropic temperature factors for these same atoms. The rings were refined as rigid units with isotropic temperature factors. The refinement converged to a final R of 0.073.

Introduction

Weakly bound complexes between metal ions and aromatic molecules have been known for some time, particularly for Ag(I).[1a] A sufficiently large number of these complexes have been isolated, characterized, and crystal structures solved to make some statements as to the factors involved in their formation. Some of these factors follow. (1) A soft metal ion, a low oxidation state, *e.g.*, Ag(I),[1] Cu(I),[2-4] Ga(I),[5] Sn(II),[6,7] Hg(I),[8] Pb(II),[9] and Tl(I).[9] This requirement is due at least in part to the fact that the higher oxidation states are such good electron acceptors that reactions involving these ions inevitably lead to reactions of the aromatic moiety, polymerization, decomposition, etc. In addition, reactions with the transition metals lead either to totally different types of benzene adducts such as dibenzenechromium or again to decomposition products. (2) The anion must be the anion of a strong acid such as ClO_4^-,[1a,c-g] $AlCl_4^-$,[1b,2,5-9] BF_4^-,[10] $F_3C_2O_2^-$,[4] and $F_3CSO_3^-$.[3] One of the functions of the anion is to decrease the lattice energy and decrease the anion-cation binding so that the complex may be more readily formed; *e.g.*, CuCl does not form a complex with benzene, but Cu(I) does with all the anions mentioned above. The other is to open the structure so that the aromatic molecule can more easily approach the metal ion. Nevertheless, several structure determinations have shown that cation-anion interactions can be important in the stabilization of these structures.[1-7] A perhaps surprising feature of many of these metal ion-aromatic complexes is that regardless of the extent of interaction between metal ion and anion, the geometry of the metal ion-aromatic complex can be correctly predicted based only upon the available s or p acceptor orbitals and the filled benzene π MO's. As part of the study of metal ion-aromatic systems, we wish to report here the preparation and crystal structure of π-$C_6H_6Pb(AlCl_4)_2{\cdot}C_6H_6$. Our purpose here is twofold, one chemical and the other structural. Although the present compound is isomorphous *vide infra* with the corresponding Sn(II) compound, it is of interest to examine in detail the changes in the M-Cl distances and in the M(II) coordination sphere in going from Sn(II) to Pb(II). In addition, the refinement of the present structure will give us a guide [since it is closely related to the Sn(II) structure] as to how well we may be able to determine the structures of known compounds such as $(HgAlCl_4)_2{\cdot}2C_6H_6$,[8] $Tl^IC_6H_6AlCl_4$,[9] and $BiCl_2AlCl_4{\cdot}C_6H_6$.[9] Although we and others have determined structures with heavy atoms, *e.g.*, Ir[11,12] or Pt,[13,14] the $MAlCl_4{\cdot}C_6H_6$

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type compounds add additional experimental problems by the necessary presence of hydrocarbon coating material on the crystals, as well as the inevitable small amount of decomposition always present due to the extreme reactivity of the $AlCl_4^-$ to traces of water vapor or oxygen.

Experimental Section

Anhydrous lead chloride, $PbCl_2$ (4.0 g, 0.014 mol), and aluminum chloride (7.0 g, 0.053 mol) were placed in one arm of an H tube under a nitrogen atmosphere. Benzene (50 ml distilled from CaH_2 under a nitrogen atmosphere) was placed in the other arm.[2b] After degassing it was distilled onto the $PbCl_2$-$AlCl_3$ 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 3 hr in an oil bath at 80°. 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 recrystallizations 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, $hk0$, $hk1$..., $hk7$, $h0l$, $0kl$, showed the crystals to be monoclinic with systematic absences $h + l = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$, establishing the space group as $P2_1/n$, a nonstandard setting of $P2_1/c$.[15]

A single crystal 0.35 mm × 0.37 mm × 0.72 mm was mounted with the long direction approximately parallel to the ϕ axis on a Picker diffractometer and aligned by variations of well-known techniques.[16] A least-squares fit[17] of the χ, ϕ, and 2θ angles of 20 reflections accurately centered on the diffractometer was used to determine the lattice constants at 23–25° (λ 0.71068 Å for Mo Kα): a = 11.365 (1) Å, b = 17.307 (2) Å, c = 12.707 (2) Å, β = 110.14 (1)°. With $Z = 4$ the calculated density is 1.99 g cm^{-3} and the observed density is between 1.7 g and 2.0 g cm^{-3} by flotation in CCl_4-bromoform solution. A more accurate value was unattainable because the crystals decompose very rapidly in halocarbon solution. The linear absorption coefficient μ was calculated to be 80.58 cm^{-1} with Mo Kα radiation. With this μ and the above crystal dimensions the variation in transmission coefficient was found to be 0.084–0.206.[18] A total of 7883 independent hkl reflections were measured by θ-2θ scan techniques with unfiltered Mo Kα radiation[19] at room temperature for 66.0 sec at 0.016°/sec, and background counts were made for 40.0 sec (B_1 and B_2). Reflections were considered absent if the integrated intensity was less than 2.5 $[(1.65)^2(B_1 + B_2)]^{1/2}$. By this criterion 2075 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. 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 6% of the total intensity, while the variation from one measurement of the standard reflection to the next was well within counting statistics, $\sigma I(\text{net}) = [I(\text{scan}) + (1.65)^2(B_1 + B_2)]^{1/2}$. 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 15% of the total integrated intensity. This was considered acceptable considering the high μ, the presence of the glass capillary, and hydrocarbon grease. The take-off angle, source-to-crystal distance, and crystal-to-counter distance were 3.7°, 18 cm, and 23 cm, respectively. The receiving aperture at the counter was 6 mm wide × 8 mm high. The half-width for an average reflection was 0.22° at a take-off angle of 3.7° indicating a mosaic spread such that all the reflection was counted during the 1.1° scan. The 0.22° 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 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.

Solution of Structure

The crystal data for π-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$ are: monoclinic, $P2_1/n$, a = 11.282 (3) Å, b = 17.317 (8) Å, c = 12.646 (6) Å, β = 110.08 (1)°, μ = 21.1 cm^{-1}. This structure was refined to a final R factor of 0.051. The close correspondence of the cell constants of Sn and Pb compounds led us to take as our starting point the atomic coordinates from the Sn structure. Three cycles of full matrix, individual atom isotropic least squares gave a conventional R of 0.11.[20] At this point we carefully examined the three-dimensional electron density and difference electron density maps. The carbon atoms were clearly resolved, albeit small, and in the correct locations for both the benzene ring bound to Pb(II) and also the benzene molecule of solvation. Since the benzene rings in the Sn structure were planar hexagonal with C–C distances of 1.39 ± 0.02 Å and the same situation appears in the present structure but with larger errors, ±0.04–0.05 Å, we decided to constrain the benzene rings to a rigid group to complete the refinement. A further five cycles of full matrix anisotropic least squares for lead, chlorine, and aluminum, with the benzene rings as rigid groups[21] and individual isotropic carbon atom temperature factors, gave 0.073 and 0.081 for R and weighted R_w.[22] The final parameter shifts were 0.10 of an esd 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.[23] The scattering factors for Pb(0), neutral chlorine, aluminum, and carbon were from Cromer and Waber.[24] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[25a] the values for $\Delta f'$ and $\Delta f''$ for lead and chlorine were those given by Cromer.[25b]

The final tabulation of observed and calculated structure factors is filed elsewhere.[26] 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 errors[27] are shown in Table II. The root-mean-square components of thermal displacements are in Table III.

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(15) F. M. Henry and K. Lonsdale, "International Tables for Crystallography," Vol. 1, Kynoch Press, Birmingham, 1952, p 99.

(16) (a) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957; (b) K. Knox, "Master Card Program for Picker Four-Angle Programmer," prepared by F. C. Carter, Picker Instruments, Cleveland Ohio, 1967, p 11; (c) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).

(17) W. A. Spofford, III, program written for the IBM 1620.

(18) Absorption correction made with program GONO-9, originally written by W. C. Hamilton, Brookhaven National Laboratory, with some local variations.

(19) Although the use of unfiltered radiation is somewhat unconventional, we have been able to demonstrate in more than one crystal structure analysis that this is a reliable means of data collection. However, one must use care in this process, especially with axial reflections and $hk0$, $0kl$, and $h0l$ data. The utility of this method depends on a number of factors such as cell dimensions, width of peaks, etc. In general, it is no worse than Zr-filtered Mo Kα radiation since this generally gives too low a background estimate at the low angle side of a reflection. We generally examine diffraction peaks from each crystal as to whether or not the unfiltered technique can be used, and if unrefined radiation is used the background is carefully scrutinized by computer for each reflection. The Mo Kβ contribution from very intense Mo Kα reflections to other reflections is computed and subtracted out when they obviously overlap. For a complete discussion and justification see R. A. Young, *Trans. Amer. Crystallogr. Assn.*, 1, 42 (1965).

Some published examples of the use of this technique are (a) G. W. Hunt and E. L. Amma, *J. Chem. Soc., Chem. Comm.*, 869 (1973), $R = 0.054$; (b) R. L. Girling, J. E. O'Conner, and E. L. Amma, *Acta Crystallogr., Sect. B,* 28, 2640 (1972), $R = 0.034$; (c) see ref 7 (two structures), $R = 0.049$ and 0.070; (d) see ref 1g, $R = 0.066$; (e) see ref 1f, $R = 0.076$; (f) there are approximately a dozen other examples both published and unpublished using this technique.

(20) Structure factor calculations and least-squares refinements were performed with a local version of "ORFLS, A Fortran Crystallographic Least-Squares Program" by W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn., ORNL-TM-305, 1962, on the IBM 7040.

(21) RIGID body refinement carried out with ORFLS-D as written by R. J. Doedens with further modifications made locally.

(22) $R = \Sigma\{||F_o| - |F_c||/\Sigma|F_o|\}$; $R_w = \{\Sigma w[|F_o| - |F_c|]^2/[\Sigma w|F_o|]^2\}^{1/2}$.

(23) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination, A Practical Guide," Collier-Macmillan, Ltd., London, 1968, p 457.

(24) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(25) (a) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964); (b) D. T. Cromer, *ibid.*, 18, 17 (1967).

(26) See paragraph at end of paper regarding supplementary material.

(27) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

Table I. Final Atomic and Rigid Group Positional and Thermal Parameters[a] and Estimated Standard Deviations

Atom	x	y	z
Pb	0.2505 (1)	0.1576 (1)	−0.1127 (1)
Cl(1)	0.0699 (8)	0.2964 (5)	−0.1554 (7)
Cl(2)	0.1130 (7)	0.1868 (5)	−0.3591 (7)
Cl(3)	0.0147 (8)	0.3814 (5)	−0.4213 (7)
Cl(4)	−0.1895 (7)	0.2504 (4)	−0.3900 (7)
Cl(5)	0.4666 (9)	0.2311 (6)	−0.3982 (8)
Cl(6)	0.4076 (8)	0.0859 (4)	−0.2288 (7)
Cl(7)	0.4082 (8)	0.2736 (4)	−0.1532 (7)
Cl(8)	0.6903 (8)	0.1850 (6)	−0.1388 (9)
Al(1)	0.0017 (8)	0.2798 (5)	−0.3310 (7)
Al(2)	0.5013 (9)	0.1947 (6)	−0.2364 (8)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb	71 (1)	30 (0)	77 (1)	−5 (1)	25 (1)	2 (1)
Cl(1)	148 (12)	48 (4)	79 (8)	23 (6)	17 (8)	−4 (5)
Cl(2)	113 (10)	53 (4)	83 (8)	30 (5)	22 (7)	−6 (4)
Cl(3)	121 (11)	38 (4)	118 (10)	−16 (5)	39 (8)	11 (5)
Cl(4)	92 (9)	37 (3)	93 (8)	−5 (4)	17 (7)	13 (4)
Cl(5)	168 (14)	78 (6)	91 (10)	−13 (7)	48 (9)	25 (6)
Cl(6)	108 (10)	34 (3)	116 (9)	−11 (5)	47 (8)	−8 (4)
Cl(7)	116 (10)	33 (3)	117 (9)	−6 (5)	56 (8)	−8 (4)
Cl(8)	93 (10)	66 (6)	164 (12)	11 (6)	13 (9)	1 (6)
Al(1)	84 (10)	34 (4)	52 (8)	−3 (5)	26 (7)	1 (4)
Al(2)	85 (11)	35 (4)	86 (9)	5 (5)	34 (8)	4 (5)

Group	x	y	z	ϕ	θ	ρ[b]
Ring 1[c]	0.1053 (13)	0.0418 (8)	−0.0685 (13)	−2.238 (15)	−2.674 (15)	1.775 (16)
Ring 2[d]	0.2570 (13)	0.0219 (10)	−0.5848 (12)	−2.164 (18)	2.913 (16)	0.527 (15)

Group	B_1	B_2	B_3	B_4	B_5	B_6
Ring 1[e]	5.1 (7)	6.3 (9)	7.8 (11)	5.4 (8)	6.7 (9)	7.4 (10)
Ring 2	6.8 (9)	9.0 (12)	7.1 (10)	8.7 (11)	9.3 (12)	6.4 (9)

Atom	x	y	z	Atom	x	y	z
C(1,1)[f]	0.1913	−0.0142	−0.0740	C(2,1)[g]	0.3469	0.0153	−0.6363
C(1,2)	0.2035	0.0206	0.0283	C(2,2)	0.3212	−0.0475	−0.5790
C(1,3)	0.1175	0.0766	0.0338	C(2,3)	0.2314	−0.0410	−0.5274
C(1,4)	0.0193	0.0977	−0.0630	C(2,4)	0.1672	0.0285	−0.5332
C(1,5)	0.0071	0.0629	−0.1652	C(2,5)	0.1928	0.0914	−0.5905
C(1,6)	0.0931	0.0069	−0.1707	C(2,6)	0.2827	0.0848	−0.6421

[a] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. [b] Angles in radians; for definition see C. Scheringer, *Acta Crystallogr.*, 16, 546 (1963). [c] Ring 1 is bound to Pb. [d] Ring 2 is the benzene of solvation. [e] B_n is the isotropic factor of C(r,n) of group r, in Å^2. [f] Carbon atoms in ring 1. [g] Carbon atoms in ring 2.

Results

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

The chlorine atoms Cl(1), Cl(2), Cl(6), Cl(3), and Cl(4) lie in a plane with the lead displaced from this plane by 0.620 (1) Å toward the bound benzene ring. The equatorial Pb-Cl distances range from 2.952 (8) to 3.218 (9) Å (chlorines 1, 2, 6, 3, and 4), while the axial distance Pb-Cl(7) is shorter at 2.854 (8) Å. These distances are somewhat long when compared to the sum of the respective covalent radii of 2.50 Å[28a] but

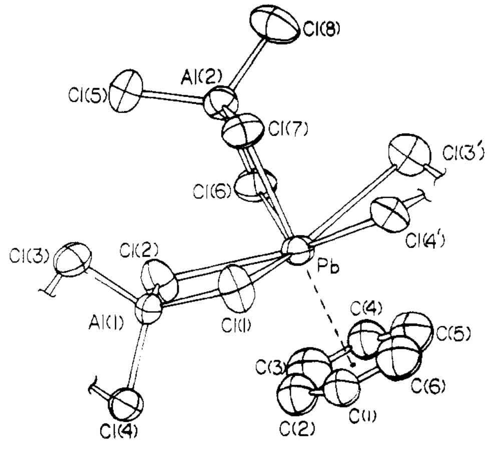

Figure 1. An ORTEP* plot of the local environment about the Pb(II) in π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$. The equatorial plane of the pentagonal bipyramid is made up of Cl(1), Cl(2), Cl(6), Cl(3'), and Cl(4'). The axial coordination sites are Cl(7) and the center of the benzene ring. The primed atoms are related crystallographically to the unprimed and constitute the repeat to form the $Pb(AlCl_4)_2$ chain. C. K. Johnson, ORTEP, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

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(28) (a) L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246; (b) *ibid.*, p 260.

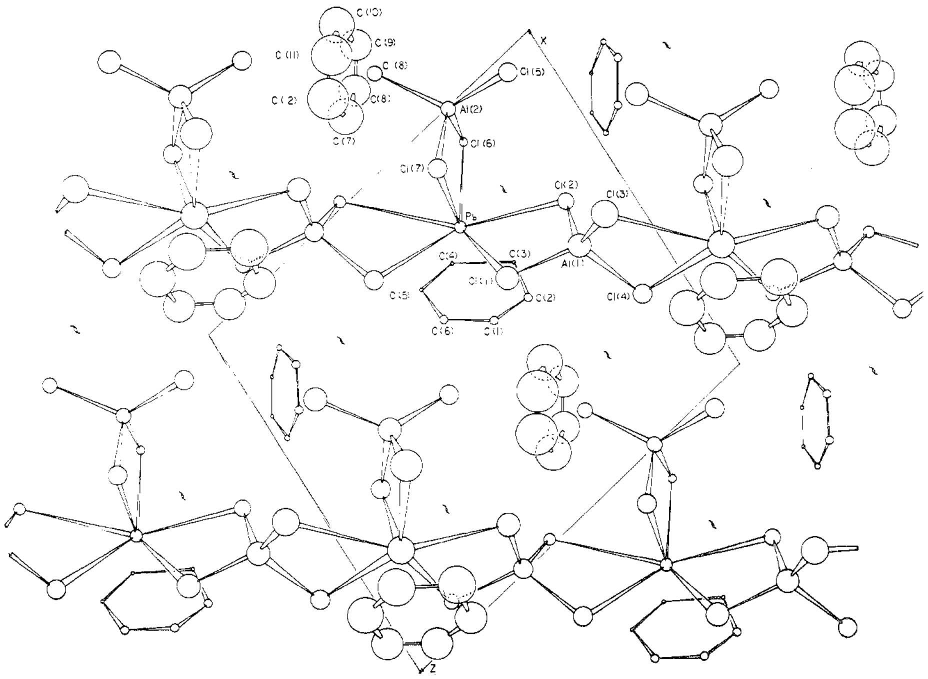

Figure 2. A packing diagram of π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$ looking up the *b* axis (*y* direction). The unit cell is shown in outline (*x* = *a*, *z* = *c*). The $Pb(AlCl_4)_2$ chain is seen to propagate almost horizontally. Carbon atoms C(1)–C(6) correspond to the benzene bound to Pb(II) whereas C(7)–C(12) correspond to the benzene of solvation.

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

	Bonded Distances		
Pb-Cl(1)	3.084 (8)	Pb-Cl(2)	3.021 (8)
Pb-Cl(3)	3.218 (9)	Pb-Cl(4)	3.111 (8)
Pb-Cl(7)	2.854 (8)	Pb-Cl(6)	2.952 (8)
Al(1)-Cl(1)	2.11 (1)	Al(1)-Cl(2)	2.15 (1)
Al(1)-Cl(3)	2.13 (1)	Al(1)-Cl(4)	2.10 (1)
Al(2)-Cl(5)	2.05 (1)	Al(1)-Cl(6)	2.18 (1)
Al(2)-Cl(7)	2.21 (1)	Al(2)-Cl(8)	2.08 (1)
Pb-C(1)	3.12 (4)	Pb-C(2)	3.13 (4)
Pb-C(3)	3.11 (4)	Pb-C(4)	3.09 (4)
Pb-C(5)	3.08 (4)	Pb-C(6)	3.10 (4)
Pb-ring center	2.77 (4)		
	Selected Nonbonded Distance Less than 4 Å		
C(1)-Cl(1)	3.74 (4)	C(2)-Cl(2)	3.76 (4)
C(3)-Cl(2)	3.98 (4)	C(4)-Cl(6)	4.03 (4)
C(5)-Cl(3)	3.77 (4)	C(6)-Cl(4)	3.64 (4)
C(4)-Cl(3)	3.82 (4)	C(7)-Cl(2)	3.70 (4)
C(7)-Cl(6)	4.02 (4)	C(8)-Cl(2)	3.75 (4)
C(8)-Cl(5)	4.03 (4)	C(9)-Cl(5)	3.99 (4)
C(8)-Cl(8)	3.92 (4)	C(8)-Cl(7)	3.84 (4)
C(1)-Cl(8)	3.83 (4)	C(9)-Cl(1)	3.91 (4)
C(1)-Cl(5)	3.79 (4)	C(11)-Cl(4)	3.78 (4)
C(12)-Cl(4)	3.76 (4)	C(11)-Cl(1)	3.87 (4)
C(12)-Cl(1)	3.82 (4)		
	Angles		
Cl(1)-Pb-Cl(2)	67.2 (2)	Cl(2)-Pb-Cl(6)	74.8 (2)
Cl(3)-Pb-Cl(6)	73.9 (2)	Cl(3)-Pb-Cl(4)	64.2 (2)
Cl(1)-Pb-Cl(4)	71.6 (2)	Cl(1)-Pb-Cl(7)	80.9 (2)
Cl(2)-Pb-Cl(7)	80.1 (2)	Cl(6)-Pb-Cl(7)	71.3 (2)
Cl(3)-Pb-Cl(7)	78.7 (2)	Cl(4)-Pb-Cl(7)	81.3 (2)
Cl(1)-Pb-ring center	102.1 (5)	Cl(2)-Pb-ring center	99.2 (5)
Cl(3)-Pb-ring center	99.2 (4)	Cl(4)-Pb-ring center	98.3 (4)
Cl(6)-Pb-ring center	107.6 (4)	Cl(7)-Pb-ring center	177.8 (4)
Cl(1)-Al(1)-Cl(2)	104.7 (5)	Cl(3)-Cl(1)-Cl(4)	105.2 (5)
Cl(1)-Al(1)-Cl(4)	111.5 (5)	Cl(2)-Al(1)-Cl(3)	112.0 (5)
Pb-Cl(1)-Al(1)	93.4 (3)	Pb-Cl(2)-Al(1)	94.4 (4)
Cl(5)-Al(2)-Cl(6)	112.4 (6)	Cl(6)-Al(2)-Cl(7)	101.0 (5)
Cl(7)-Al(2)-Cl(8)	109.3 (6)	Cl(5)-Al(2)-Cl(8)	115.1 (6)
Pb-Cl(3)-Al(1)	90.8 (4)	Pb-Cl(4)-Al(1)	94.3 (4)

Table III. Root-Mean-Square Displacements along Principal Axes of the Thermal Ellipsoid (Å)

Atom	Axis 1	Axis 2	Axis 3
Pb(1)	0.194 (2)	0.219 (2)	0.239 (2)
Cl(1)	0.23 (1)	0.24 (1)	0.34 (1)
Cl(2)	0.21 (1)	0.24 (1)	0.33 (1)
Cl(3)	0.21 (1)	0.28 (1)	0.31 (1)
Cl(4)	0.22 (1)	0.22 (1)	0.29 (1)
Cl(5)	0.22 (1)	0.31 (1)	0.37 (1)
Cl(6)	0.21 (1)	0.25 (1)	0.29 (1)
Cl(7)	0.22 (1)	0.24 (1)	0.30 (1)
Cl(8)	0.22 (1)	0.32 (1)	0.37 (1)
Al(1)	0.19 (2)	0.22 (1)	0.23 (1)
Al(2)	0.21 (1)	0.23 (1)	0.25 (0)

should be considered as real covalent interactions since the sum of the van der Waals radii is 4.0.[28b] A lead(IV)-chlorine distance of 2.46 (2) Å in the vapor phase of $PbCl_2$ has been reported.[29]

The Cl(equatorial)-Pb-Cl(equatorial) bond angles vary from 64.2 (2)° to 74.8 (2)°, while the ideal value for these angles based on a regular pentagon is 72.0°. The smallest values in the series [Cl(1)-Pb-Cl(2), 67.2 (2)°; and Cl(3)-Pb-Cl(4), 64.2 (2)°] occur when the chlorine atoms are bound to the same aluminum atom, and one would expect such a distortion to be observed.

The lead-carbon distances average 3.11 Å with individual deviations of ±0.04 Å or less, indicating a symmetrical interaction between lead and carbon. The lead to ring center distance is 2.77 (4) Å with a ring center-Pb-Cl(7) angle of 177.8 (4)°. The ideal bond angle for pentagonal bipyramid geometry would be 180°.

A lead-carbon distance of 2.27 (3) Å has been found in $[\pi\text{-}C_5H_5Fe(CO)_2]_2Pb(CH_3)_2$,[30] while distances of 2.20 to 2.25 Å have been reported for $[(C_6H_5)_2BrPb]_4C$.[31] An electron diffraction study of $(\pi\text{-}C_5H_5)_2Pb$ has shown Pb-C

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(29) M. W. Lister and L. E. Sutton, *Trans. Faraday Soc.*, **37**, 393 (1941).

(30) B. P. Biryukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Zh. Strukt. Chem.*, **9**, 922 (1968); *Chem. Abstr.*, **70**, 15111f (1969).

(31) J. Kroon, J. B. Hulscher, and A. F. Peerdeman, *J. Organometal. Chem.*, **23**, 477 (1970).

Table IV. Comparison of Pb-X and Sn-X Distances (Å)

	Pb	Sn
M-Cl(1)	3.084 (8)	3.020 (2)
M-Cl(2)	3.021 (8)	2.907 (2)
M-Cl(3)	3.218 (9)	3.280 (2)
M-Cl(4)	3.111 (8)	3.145 (2)
M-Cl(6)	2.952 (8)	2.881 (2)
M-Cl(7)	2.854 (8)	2.766 (2)
M-C(av)	3.11 (4)	3.06 (1)

distances of 2.78 (2) Å. While a Pb-C distance of 3.11 (4) Å in π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$ is long when compared to lead-methyl carbon distances, it is similar to the Pb-C distance found in $(\pi\text{-}C_5H_5)_2Pb$. The long lead-carbon distances and the displacement of the lead from the plane containing the five chlorine atoms (Table III) toward the benzene ring can be considered to arise from the steric constraints imposed by the chelated $AlCl_4^-$ groups and the van der Waals repulsion between the chlorine and carbon atoms. The bond distances and angles for the tetrachloroaluminate ions show the expected values.

Table IV shows a comparison of the Pb-C, Sn-C, and Pb-Cl, Sn-Cl distances. Although there exist substantial differences between Pb-Cl and Sn-Cl distances, particularly Pb-Cl(6), Sn-Cl(6) and Pb-Cl(2), Sn-Cl(2), there do not seem to be systematic differences that can be readily rationalized. On the other hand, the Pb-C and Sn-C distances are not significantly different.

Discussion of Bonding

Any discussion of the chemical bonding between Pb(II) and its neighboring atoms must rationalize the following facts: (1) the relatively long Pb-Cl distances; (2) the C_{6v} symmetry of the Pb-benzene interaction; (3) the relatively long Pb-C distances. 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 Pb(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 6d levels are approximately 18.7 eV[32] above the 6s compared to 7.5 eV for the 6s-6p separation. The inclusion of these d orbitals again would not materially affect the description. Pb-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.[33] 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.

The molecular orbitals for the benzene, Pb(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 Pb(II) and benzene. The next grouping of energy levels are those between chlorine and Pb(II) with most likely the totally symmetric a_1 MO's being lowest. One of these is the Pb(6p)-Cl σ axial interaction while the other is a totally symmetric framework MO involving the Pb(II) (6s) and the equatorial halogen σ orbitals. e_1' involves the Pb(II) $6p_x$, $6p_y$, and halogen σ orbitals whereas e_2 is a nonbonding MO involving only chlorine. The next level is a_1''', probably mostly Pb(II) 6s 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'''.

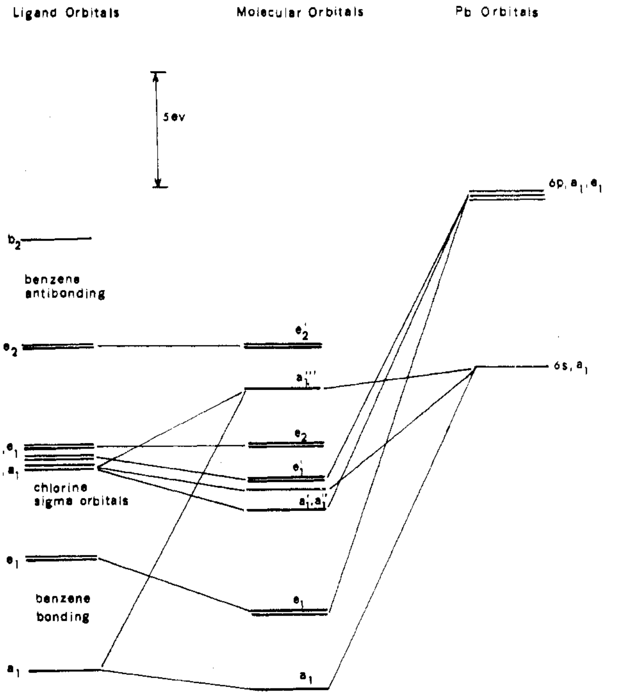

Figure 3. A qualitative molecular orbital energy level diagram for the interaction of Pb(II) with the seven ligands; six Cl and one benzene. The ordering of the MO levels involving halogen may be different from that depicted, but it would not change the arguments in the text. The antibonding levels above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

Since the principal interaction between Pb(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 Pb-C distance is long. Furthermore, the interaction between $6p_x$, p_y and benzene e_1 would give rise to the C_{6v} Pb(II)-C_6H_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 Pb-Cl bonding MO's, that means that there are only eight bonding electrons for six chemical bonds and these Pb-Cl bonds must be long in comparison to normal Pb-Cl single bonds.

This description of the bonding in π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$ 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.

If this description of the bonding particularly between Pb(II) and benzene[34] is valid, then some interesting predictions can be made. For example, a Pb(II)-olefin complex

(32) C. E. Moore, *Nat. Bur. Stand.* (*U. S.*) *Circ.*, 467, 213 (1958).

(33) E. M. Schustorovich and M. E. Dyatkina, *Dokl. Akad. Nauk. SSSR*, 128, 1234 (1959).

with the Pb placed equidistant from the carbon atoms should not exist since the acceptor 6p orbital of Pb(II) would not belong to the same symmetry species as the donor π orbitals of the olefin. No such complexes are known, and we have not yet succeeded in synthesizing them with either Sn(II) or Pb(II). On the other hand, such a complex should be possible with the Pb(II) placed equidistant between carbons 2 and 3 of butadiene. Experiments are currently underway to prepare such compounds.

In this structure Pb-Cl bonds are weakened to form the fourth Al-Cl bond in $AlCl_4^-$. On this basis one would expect anhydrous $PbCl_2$ to behave as a moderating cocatalyst in $AlCl_3$-catalyzed alkyl halide Friedel-Crafts reactions but have little effect in $AlCl_3$-catalyzed acyl halide reactions. Unfortunately, there is no direct experimental data on this point either way.[35]

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Regristy No. π-$C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$, 52003-11-9.

Supplementary Material Available. A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2429.

[34] If the aromatic-metal interaction is considered alone the binding can be considered in terms of charge-transfer theory; see R. S. Mulliken, *J. Amer. Chem. Soc.*, 74, 811 (1952).

[35] G. A. Olah, "Freidel Crafts and Related Reaction," Vol. 1, G. A. Olah, Ed., Interscience, New York, N. Y., 1963, p 259.

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Chromium-Carbon Bonds in Aqueous Solutions. A Pulse Radiolytic Study

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The specific rates of reaction of 16 aliphatic radicals with $Cr(H_2O)_6^{2+}$ were determined. The absorption spectra due to the chromium-carbon bonds in the products of these reactions were measured. The specific rates of aquation of these complexes as a function of pH were determined. The effects of the structure of the aliphatic radicals on these spectra and specific rates of reactions are discussed in detail. It is shown that chromium induces water elimination when a β-hydroxyl group is present.

The products of reaction of a series of carbon free radicals with several transition metal complexes in their lower oxidation states were shown to contain carbon-to-metal bonds.[1] The specific rates of reaction of several aliphatic radicals with $Cr(H_2O)_6^{2+}$ in aqueous solutions were recently measured, using the pulse radiolytic technique.[2] It was suggested that a major factor in determining the specific rate of this reaction is the probability of locating the unpaired electron on a given carbon atom. It seemed of interest to check this conclusion by measuring the specific rates of reaction of a larger series of free radicals with $Cr(H_2O)_6^{2+}$.

Further it seemed that the pulse radiolytic technique might permit observation of the uv spectra of such chromium-carbon compounds $Cr^{III}(H_2O)_5RH$. Because of the experimental techniques used in other studies,[1b,f] the spectra of only relatively stable compounds were reported, and for most of them, only at $\lambda > 300$ nm. We hoped that measurement of a large series of such compounds would help in elucidating the origin of the bands due to the chromium-carbon bonds.

Finally, it seemed of interest to study the kinetics of the cleavage reaction of the chromium-carbon bonds. The data available suggest that the mechanism of this reaction is heterolytic or homolytic for different chromium-carbon compounds.[1c,f,3]

Experimental Section

Materials. All organic solutes used were reagent grade chemicals, supplied by Fluka, Merck, or Hopkin Williams, and were used without further purifications. The perchloric acid used, 70% $HClO_4$ Pro-analysis, was supplied by Merck. All the water used was triply distilled.

Chromium(II) perchlorate solutions were prepared by dissolution of Spectrograde chromium metal, Johnson Matthey, in 1.0 *M* $HClO_4$ under an argon atmosphere. When solutions at pH >2 were required, excess chromium metal was introduced into 0.2 *M* $HClO_4$. These solutions were diluted after no further hydrogen evolution was observed. The pH's of the latter solutions were measured under an argon atmosphere. The vessel used is shown in Figure 1. The argon used was bubbled through a washing bottle containing a concentrated $Cr(ClO_4)_2$ solution before it entered the reaction vessel. The argon was bubbled through the 5/20 ground joint A into the solution while stopcock B was closed and stopcock C was open. The solutions thus prepared contained $(2-100) \times 10^{-3}$ *M* Cr_{aq}^{2+} and less than 5% of Cr_{aq}^{3+} as determined by the epr technique.

Procedure. The chromium(II) solutions were transferred into 100-ml all-glass syringes (joined to the preparation vessel at the ground joint A) by applying argon pressure through stopcock B while stopcock C was closed. Portions of 5-20 ml of these chromium(II) solutions were transferred into another 100-ml syringe containing a deaerated argon-saturated solution of the required organic solute and perchloric acid. These solutions were transferred into the irradiation cells.

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