Crystal Structure of Diphenyllead-Dichloride

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Diphenyllead-dichloride $(C_6H_5)_2PbCl_2$, crystallizes in the orthorhombic system, space group $Pnnm = D_{2h}^{12}$, $a = 17.965 \pm 0.005 \text{ Å}, \quad b = 8.565 \pm 0.003 \text{ Å}, \quad c =$ 4.005 ± 0.003 Å, Z = 2. The crystal structure, determined by two-dimensional X-ray analysis, is characterized by polymeric chains of the type

Pb < Cl Pb < Pb < parallel to the c axis and with

equivalent Pb-Cl bonds mutually perpendicular. The phenyl rings are normal to the chain axis, with the Pb-C bonds nearly perpendicular to the plane of the chain; the lead atoms are therefore octahedrally coordinated. The character of the Pb-Cl and Pb-Cbond and the packing of the chains in the crystal are discussed.

Introduction

Although many investigations have been reported in recent years on the chemistry of alkyl- and aryl-lead cations and their adducts with electron-pair donors.¹⁻⁴ very little is known on the structure of organo-lead compounds. It seemed therefore worth-while to carry out the X-ray crystal structure analysis of some of them. and the phenyllead-chlorides were preferred to the methyl and ethyl derivatives, owing to their relatively greater stability to light and radiations; moreover, it was expected that the larger contribution of the phenyl groups to the diffraction amplitudes and the known ring conformation would result in a more accurate determination of the light atom positions. Main interest was in fact in the type and symmetry of metal coordination and in the length and character of both metal-carbon and metal-chlorine bonds.

In this paper, the results obtained by X-ray analysis of diphenyllead-dichloride are reported.⁵

Experimental Section

Crystallization from benzene solution, at room temperature, gave long transparent needles with rectangular cross-section. The crystals were examined in

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Weissenberg and precession cameras, using CuKa (Ni-filtered) and MoKa (Zr-filtered) radiations respectively, with the oscillation axis parallel to the needle (c) axis. Reflections occurred under the following conditions: (Okl) only if k+l=2n, (hOl) only if h+l=2n; the diffraction symbol mmmPnn- corresponds to the orthorhombic space group $D_{2h}^{12} = Pnnm$ (centro-symmetryc) or $C_{2v}^{10} = Pnn2$ (non-centrosymmetric); subsequent analysis showed the first to be the actual case. Physical and crystallographic data are collected in Table I.

Table I. Physical and crystallographic data for (C6H3)2PbCl2

M.W. = 432.3M.P. = $284 \div 286^{\circ}$ C (with decomposition) Crystallographic system: orthorhombic Space group $D_{2h}^{12} = Pnnm$ Unit cell parameters: $a = 17.965 \pm 0.005$ Å $b = 8.565 \pm 0.003 \text{ Å}$ $c = 4.005 \pm 0.003 \text{ Å}$ $V = 616.3 \text{ Å}^3$ Z = 2; F(000) = 396 $d_{calc} = 2.33 \text{ g cm}^{-3}$ $d_{obs} = 2.28 \text{ g cm}^{-3}$ (by flotation) $\mu_{C_{U}K_{\alpha}} = 311 \text{ cm}^{-1}$; $\mu_{M_{0}K_{\alpha}} = 161 \text{ cm}^{-1}$

For the structure analysis, 153 independent hk0 reflections, out of 202 possible, were observed on Weissenberg photographs (multiple film technique); all the 62 hOl possible reflections were measured on precession photographs ($\mu = 30^{\circ}$). Freshly prepared crystals were used to avoid the appearence of drawing out and compaction of spots, observed for the hk0 reflections from aged crystals and presumably arising from slight chemical decomposition.

Integrated intensities were obtained with a record-Non-linear behaviour of the ing microdensitometer. X-ray films used (Ilford, Industrial G) was accounted for^{6,7} and the usual Lorentz and polarization factors applied.

Structure determination. The space group symmetry requires the lead atoms to be packed in a bodycentered lattice.

The (001) projection, which has pgg symmetry in both Pnnm and Pnn2 space groups, was examined first; the corresponding Patterson map (Figure 1) clearly showed the Pb-Cl and the Pb-C vectors and the approximate x and y coordinates so obtained were

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refined by Fo and ΔF syntheses. As a result, carbon atoms appeared to be localized in a regular hexagonal arrangement (see bond lengths and angles reported below in Table VI).



Patterson map, (001) projection. Figure 1. Contours are drawn at equal but arbitrary intervals, except for the origin peak, where the drawn contours are at quadruple intervals. $Pb-Cl (\blacksquare)$ and Pb-C (x) vectors, derived from final coordinates, are indicated.

Their position was however more precisely determined, first, by rotating the whole phenyl ring by a few degrees about the c axis, and secondly, by varying the phenyl-to-lead distance. A minimum R factor was observed at an angle α of about 42° between the Pb-C₁ direction and the a axis, and at a Pb-C₁ distance of 2.12 Å, respectively.

The three-dimensional arrangement of atoms is controlled by diad axes parallel to c, which relate pairs of atoms in each molecule; therefore, they must have the same z coordinate, which must be zero or 1/2, if the highest crystal symmetry Pnnm is obeyed, or any other value if the space group is Pnn2. For the Pb and Cl atoms, the two possible arrangements are shown in Figures 2a and 2b, respectively.



Figure 2. Possible arrangements of Pb and Cl atoms.

The Patterson projection along [010] (Figure 3) was consistent with the highest symmetry hypothesis a); the chlorine atoms of the molecule at the origin were



Patterson map, (010) projection. Contours are Figure 3. drawn at equal, but arbitrary intervals.

further confirmed to lie on the mirror plane at $z = \frac{1}{2}$ by hol structure factor calculations and by difference Fourier maps, where no significant anisotropic electron density distribution was observed for the chlorine atoms.

However, hol structure factors were also calculated for arrangement b), and the corresponding R values are plotted in Figure 4 vs. the Cl distance from the mirror plane at $z = \frac{1}{2}$ (white circles; upper scale); the R factor did not rise so sharply and suddenly as it could be expected, but this was not assumed as a supporting evidence for a shift of the chlorine atoms, that is, for the rather unreliable arrangement b), mainly because no definite minimum at a significant distance was observed.



Variation of the R factor for hol reflections by Figure 4. moving the Cl atom away from mirror plane (white circles, upper scale) and by rotating the phenyl ring about the $Pb-C_1$ bond (black circles, lower scale).

The arrangement shown in Figure 2c has been found in very similar structures, like dipyridine-copperdichloride8 and dipyridine-mercury-dichloride9; however, it would require a monoclinic symmetry, and was disregarded after both the hypotheses of a pseudo-

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orthorhombic cell and of twinning (of the type described by Dunitz⁸) were taken into consideration.

A deviation from the highest symmetry might also result from a rotation of the two phenyl rings about the Pb-C bonds out of the ab plane and by the same amount; this rotation, which would not change the metal coordination, is more difficult to ascertain because it is not clearly detectable in the ac electron density map, where light atoms overlap. Yet, it was excluded on the basis of the regular hexagonal arrangement of carbon atoms observed on the ab projection, as well as by hol structure factor calculations: variation of the corresponding R factor as a function of the rotation angle φ is shown in Figure 4 (black circles; lower scale). Although a few degree rotation would be allowed, no positive indication is observed and we concluded that carbon atoms too lie on mirror plane; this point is further discussed below.

Table II. Atomic coordinates and temperature factors

	x/a	y/b	z/c	B(Å ²)
Pb	0.0000	0.0000	0	2.65; 2.15
Cl	0.0765	0.1615	1/2	3.10
C_1	0.0876	0.1662	0	6.00
C ₂	0.0709	-0.3259	0	5.00
C ₁	0.1293	-0.4367	0	4.50
C.	0.2044	-0.3879	0	3.00
C.	0.2220	-0.2271	0	3.50
Č,	0.1636	-0.1163	0	3.50

Table III. Observed and calculated hk0 structure factors ($\times 10$). Unobserved reflections, marked by an asterisk, have been given half the minimum observed intensity value

	ĸ	F ₀	F,	н	ĸ	if _o i	F _c	н	ĸ	F ₀	Fc		ĸ	(F ₀)	٢
,	•	1675	1655	17	2	229	-198	3	5	850	820	13	,	428	429
	Ň	807	977	18	2	477	427	4	5	206	172	14	7	60-	- 37
6	ŏ	617	640	19	2	65=	-12	5	5	842	792	15	1	355	353
8	ō	573	675	20	2	393	393	6	5	62=	20	16	7	84	- 5 5
10	0	935	1004	21	2	51=	34	,	5	657	570	17	1	233	247
12	0	968	982	1	3	750	756	8	5	172	-130	18	7	20 =	-8
14	0	946	944	2	3	225	195	9	5	703	756	0	8	501	470
16	0	572	518	3	3	1142	1242	10	5	108	-63	1	8	73.	-86
18	0	387	350	4	3	197	-169	11	5	606	570	2	8	445	399
20	0	292	Z17	5	з	1316	1412	12	5	111	-101	3	8	169	-131
22	0	235	Z26	6	3	131	-101	13	5	501	514	4	8	558	521
1	1	1715	1652	7	3	1140	1201	14	5	72=	34	5		157	-101
2	۱	290	210	8	з	202	115	15	5	493	480		8	539	518
3	١	1565	1494	9	з	879	919	16	5	95	93		8		20
4	ı	492	-504	10	3	61 -	3		5	385	307				
5	1	819	1102	11	3	633	598	18	5	86	79	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		767	177
6	1	99	88	12	3	- 88	44	20	2	284	200	11		87	109
7	1	839	977	13	3	428	392	20	2	1072	016	12	A	315	303
8		12.	10	14	3	72.	- 55	,		64.	32	11	8	53#	5
. 9	!	742	818	15	3	513	487	;	6	1048	968	14	× 8	266	262
10		249	235	10		/3.	444	÷	6	650	- 6 2	16	ā	67	-65
		116	900	10		*50	- 21	, i	6	660	595	16	8	200	211
12		881	883	10		445	450		6	130	116	1	9	370	314
14	;	30.		20			11	6	6	420	377	2	,	684	- 31
15	i	568	\$24	21	â	332	340	7	6	70=	-20	,	,	393	349
16	i	112	-108	22	3	32 .	02		6	419	403	4	,	66-	-47
17	1	457	462	0	4	733	633	9	6	126	-83	5	9	444	441
18	1	136	-86	1	4	48*	-8	10	6	525	542	6	9	63*	2
19	1	379	340	2	4	884	919	11	6	73=	46	7	9	461	465
20	1	61=	41	3	4	325	292	12	6	597	648	8	9	58*	18
21	1	292	269	4	4	1111	1151	13	6	71-	-41	,	9	349	334
22	1	44-	36	5	4	303	215	14	6	503	500	10	9	52*	25
23	,	240	245	6	4	999	1007	15	6	65+	38		9	234	213
0	2	899	935	7	4	101	35	16	6	350	361	12	9	41.	11
1	2	321	-282	8	4	968	1022	17	6	53*		13	. 9	210	207
2	2	1089	1232	,	4	229	-203	18	6	238	205	0	10	286	252
3	2	470	-461	10	4	726	672	19	•	34.	-8		10	35*	
4	2	1048	1188	11	4	252	-224	1	'.	849	/4/		10	290	636
5	2	406	- 360	12	1	485	467		4	109	-122	:	10	145	117
6	2	1256	1523	13	1	93	423	3	΄,	72.	505		10	50+	32
	2	1040	1205		2	77-	80		έ,	508	413	6	10	333	359
	2	120	284	14	2	472	420		,	146	-87	ž	10	44=	-12
,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	-	330	204	10	-	96	94	,	,	513	472		10	235	288
10	-	128	010	18		452	415		,	73.	67	9	10	34=	-27
12	2	641	592	19		56 *	31	9	7	427	406	10	10	200	239
11	\$	142	141	20	4	323	312	10	7	72=	76	1	11	220	246
14	2	484	489	21		37 -	-20	11	7	466	480	2	11	25 -	61
15	2	103	-104		5	1034	972	12	7	104	40	3	11	198	243
16	;	551	536	2	5	232	172								

Final coordinates and individual isotropic temperature factors are listed in Table II; for the Pb atom, the two values B = 2.65 and 2.15 Å² were applied to hk0 and h0l reflections, respectively, whose observed and calculated structure factors are collected in Tables III and IV. R factors are reported in Table V.

Table IV. Observed and calculated hol structure factors $(\times 10)$; all of them have positive sign

н	L	F ₀	F _c	н	L	1501	۴٤	K	L	F ₀	F _c	H	t	F ₀	F _c
Ż	0	1521	1567	9	۱	1029	1077	16	2	518	483	0	4	633	733
4	0	834	951	11-	1	764	728	18	z	318	314	z	4	511	579
6	0	653	632	13	1	626	631	20	z	242	241	4	4	333	397
8	0	622	707	15	1	561	550	22	2	239	252	6	4	256	289
10	0	971	1031	17	1	527	516	1	3	688	714	8	4	271	309
12	0	1015	1082	19	1	668	469	3	3	669	616	10	4	395	404
14	0	1030	963	21	1	504	373	5	3	796	741	12	4	372	449
16	0	723	594	23	1	454	292	,	3	707	586	14	4	296	394
18	0	482	378	0	z	1870	1871	9	э	630	616	16	4	304	274
20	0	245	Z82	2	2	1238	1161	11	3	431	490	1	5	Z 5 0	329
22	0	239	302	4	2	884	762	13	3	531	430	3	5	250	303
24	٥	286	303	6	2	626	534	15	з	396	377	5	5	191	295
1	1	1542	1470	8	2	543	561	17	3	318	344	7	5	207	280
3	1	861	825	10	2	771	772	19	3	358	304	9	5	169	267
Ś	1	1263	1495	12	2	811	841	21	3	260	250	17	5	250	246
7	1	1181	1209	14	2	786	749								

Table V.

R factors for observed reflections; R* includes unobserved. (a) Reflections with h+k+l=2n and F_c with the Pb contribution only. (b) Amplitudes calculated with Pb and Cl contributions only. (c) Final values.

Reflections		(a)	(b)	(c)		
hk0	R P*	18.0	12.2	8.7		
h01	R	22.3	16.5	9.4		

Standard deviations of x and y coordinates (Cl, 0.006 Å; C, 0.02 Å) were estimated by Cruickshank's relations^{10,11}; atomic scattering factors by Forsyth and Wells¹² were used, and allowance made for Pb anomalous dispersion.¹³

Calculations were performed by an Olivetti Elea 6001 computer, using the programs by the Centro di Strutturistica Chimica del C.N.R.¹⁴

Results and Discussion

Bond lenghts and angles in diphenyllead dichloride are reported in Table VI, together with estimated standard deviations. Each Pb atom is octahedrally coordinated to four Cl and two C atoms, and the octahedra share two opposite edges, thus forming polymeric chains parallel to the c axis (Figure 5), in which the $Pb \xrightarrow{Cl} Pb$ bridge is nearly a square

(88.5° at the Pb atom) and the two Pb-C bonds are about normal to the plane of the chain (87.3°).

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Table VI. Interatomic distances and angles, with standard deviations. Cl₁ and Cl₂ in the equivalent positions \bar{x}, \bar{y}, z and $\overline{x}, \overline{y}, \overline{z}$, respectively

Pb-Cl	2.795±0.006 Å	Pb-Cl-Pb	$91.5 \pm 0.2^{\circ}$
$Pb-C_1$	2.12 ± 0.02	$Cl-Pb-Cl_1$	$88.5 \pm 0.2^{\circ}$
$C_1 - C_2$	1.40 ± 0.03	$C_1 - Pb - Cl$	$88.1 \pm 0.5^{\circ}$
$C_2 - C_3$	1.41 ± 0.03	$C_1 - Pb - Cl_2$	$91.9 \pm 0.5^{\circ}$
C ₃ −C ₄	1.41 ± 0.03	$Pb-C_1-C_2$	119.8±1.2°
C4-C5	1.41 ± 0.03	$C_1 - C_2 - C_3$	$119.8 \pm 1.4^{\circ}$
Cs-C6	1.41 ± 0.03	$C_2 - C_3 - C_4$	120.7±1.4°
$C_6 - C_1$	1.43 ± 0.03	$C_3 - C_4 - C_5$	$120.2 \pm 1.4^{\circ}$
$Cl - Cl_t$	3.90 ± 0.01	$C_4 - C_5 - C_6$	119.2±1.4°
		$C_5 - C_6 - C_1$	$120.5 \pm 1.4^{\circ}$
		$C_{6} - C_{1} - C_{2}$	$119.8 \pm 1.4^{\circ}$



Figure 5. Perspectic view of the (C₆H₅)₂PbCl₂ chain.

A perspective view of the crystal packing is shown in Figure 6: two polymeric chains cross the unit cell and are shifted by $\frac{1}{2}$ c from each other; lead and chlorine atoms of the chain at the origin lie in a plane parallel to c and rotated by 45.2° counter-clockwise from the *a* axis direction, being therefore tilted by 1.5° only from the (210) crystallographic plane. The hydrogen atom positions were calculated assuming C-H, 1.08 Å; intermolecular distances are reported in Figure 7.

The strand structure is characterized by Pb-Cl bonds of 2.80 Å, which should be regarded as essentially ionic.

Distances of the same order have been reported for compounds of divalent lead with distorted coordination seven,^{15,16} but no crystal structure of organo-lead compounds similar to the present one is reported in the literature.

As a matter of fact, the sum of covalent radii of Cl (0.99 Å) and Pb (tetrahedral, 1.46 Å; octahedral,

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Packing of the polymeric chains in the unit cell. Figure 6.



Crystal packing viewed along the c axis; inter-Figure 7. atomic contacts up to 4.50 Å are indicated.

1.50 Å)¹⁷ would give a much shorter bond length, in agreement with the values found in covalently bonded compounds.^{18,19,20} A square arrangement of four covalent Pb-Cl bonds of 2.50 Å would give normal approach between both chlorine and lead atoms, so allowing a stronger interaction (3.6 Å) between phenyl rings too. Loosening of the square arrangement of chlorine atoms and lengthening of Pb-Cl bonds to 2.80 Å is therefore not due to Pb-Pb nor to Cl-Cl interactions, for which much shorter contacts have been reported (Pb-Pb: 3.38 Å²¹ and 3.50 Å²²; Cl-Cl: $3.18 \div 3.40$ Å in similar chain structures^{8,23,24}).

A description of the diphenyllead-dichloride structure by ionic Pb-Cl bonds requires a Pb ionic radius of 0.99 Å (Cl, 1.81¹⁷). A similar value ($R_2 = 0.95$ Å) is also obtained by the equation $R_2 = R_1 \cdot Z^{2/(n-1)}$, using an "ionic univalent radii" $R_1 = 1.08$ and a Bohr exponent n = 12.¹⁷

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On the other hand, by substracting from the distances observed in the crystal structure of several Pb compounds^{16,20,21,25-37} the known ionic radii of the bonded atoms, a mean value is obtained for the Pb ionic radius, which is 1.20 Å (corrected to 1.1 Å for the high radius ratio limit³⁸) from the F, Cl and Br compounds of Pb²⁺, which have coordination number higher than 6,16,25-28 while 1.05 Å is obtained from the less electronegative I, S, Se and Te derivatives^{29,33} of Pb²⁺, and 0.76 Å from the Pb⁴⁺ compounds.^{20,21,34-37}

The empirical ionic radius of hexacoordinated lead is therefore expected to range approximately from 1.1 Å for Pb^{2+} to 0.8 Å for Pb^{4+} ; the actual value will depend upon several factors besides the formal oxidation state, e.g., type and electronic distribution of surrounding atoms, radius ratio, crystal symmetry. The intermediate value of 0.99 Å seems therefore quite reasonable.

Finally, a fractional covalent bond number n = 0.20, i.e., an 80% ionic character in the Pb-Cl bonds (leaving a formal charge of +1.6 on lead atoms) is obtained by the Pauling's equation,¹⁷ $D_n = D_1 - 0.60 \log n$, using a covalent bond length, D₁, corrected from 2.49 to 2.39 Å for the difference in electronegativities.³⁹

Therefore, we can conclude that Pb-Cl bonding in the present structure is essentially ionic in character.⁴⁰

Two Pb-C bonds of 2.12 Å complete the Pb octahedral coordination. This length is slightly shorter than the few values reported in the literature : 2.25 ± 0.06 Å in Pb₂(CH₃)₆,⁴³ 2.203 ± 0.010 Å in $Pb(CH_3)_{44}^{44}$ and 2.19 ± 0.03 Å in $Pb(C_6H_5)_{4.45}^{45}$ These values, which refer to molecules with tetrahedral coordination, agree with the sum of covalent radii, which give 2.23 Å, or 2.17 Å if allowance is made for difference in electronegativities.39

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A shorter Pb–C value points out a partial π bonding between phenyl and lead, that is, resonance between the two aromatic rings "through" the metal atom. This is also supported by the coplanarity of the rings. Both phenyl groups lie, in fact, in the plane normal to the chain direction (Figure 5), thus differing from the very similar structures of Mn,46 Co,8 Cu8 and Hg9 dipyridine dichlorides, which show some tilt of the pyridine rings, besides asymmetric chlorine bridges. In these structures, which have shorter chain repeats (3.73, 3.66, 3.87 and 3.80 Å, respectively) a small tilt allows stronger interactions between the rings along the chain and better interchain approaches in the crystal packing. In diphenyylead dichloride, a satisfactory approach of the aromatic rings along the chain, say 3.6 Å, would require a tilt of more than 25°, and though a small tilt (5-10°; see Figure 4) could be possible, no evidence was given by structure factor calculations and Fourier syntheses; moreover, the short distance observed between each chlorine and the carbon atoms in the orthoposition (3.48 Å) would be further reduced by tilting.

On the contrary, untilted phenyl groups give rise to the very symmetric arrangement shown in Figure 5, in which hydrogen atoms in the ortho-position lie at the corners of a rectangular prism, nearly a cube, with the Cl atoms about at the centres of two opposite faces.



Figure 8. Outline of the Cl atom environment. The plane π of the paper, parallel to the c axis, is perpendicular to the Cl-Cl line and contains the Cl atom. H ator by the molecule numbering shown in Figure 7. H atoms are identified () distances from π ; [] distances from the Pb-Cl-Pb plane.

A more detailed outline of the Cl atom environment is reported in Figure 8: eight hydrogens surround each chlorine atom at about 3.1 Å, which is the normal Van der Waals distance, so that all the five hydrogen atoms of each phenyl group are involved in these contacts.

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