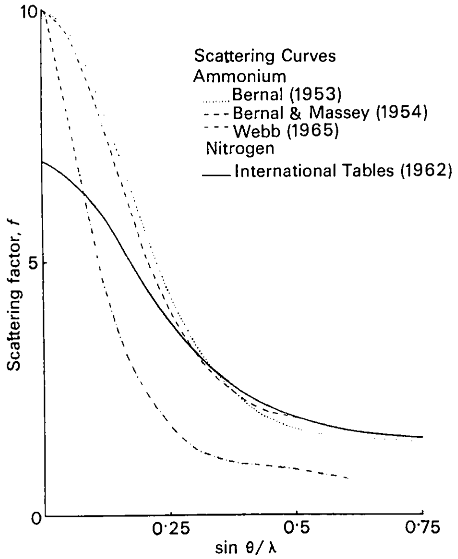

Fig. 1. Scattering curves for ammonium and nitrogen.

values of sin θ/λ. This would be expected; electrons further away from the central nucleus seem to have little effect on the scattering factor at high values of sin θ/λ. This may be easily seen by reference to the atomic scattering factors in *International Tables* (1962), where atomic scattering factors for neutral and ionized atoms differ little at larger values of sin θ/λ. The errors in the present scattering factors are unknown but the calculation for sin $\theta/\lambda=0$ gives 9·998 and 10·001 for the values from the wave functions of Bernal (1953) and Bernal & Massey (1954) respectively compared with the correct value of 10·000, so the errors are probably in the third decimal place. This, of course, assumes that the N–H distances of 0·97 Å for which the wavefunctions were calculated is correct. The effect of a different N–H distance on the wavefunctions and hence on the scattering factors is not known.

Webb's (1965) figures were thought to be due to taking the abscissae of Banyard & March's (1961) curve to be in Å whereas they are in atomic units. However, a check calculation based on this gave moderate agreement at low values of sin θ/λ but very poor agreement at larger values of sin θ/λ. So this assumption cannot be entirely correct.

The scattering curves for ammonium found in the present investigation are very similar although there are differences of up to 10% in individual values. These differences are hardly likely to be important for most work but may cause errors in high accuracy work.

According to Banyard & March (1961) a comparison of the electron distribution curve for ammonium with that for methane suggests that the figures of Bernal & Massey (1954) are the more accurate and for this reason the scattering curve for ammonium taken from their figures is probably the best.

The scattering factor for ammonium has been determined experimentally from intensity measurements on ammonium chloride (Wyckoff & Armstrong, 1930). However, subsequently it has been shown, from infrared spectroscopy (Wagner & Hornig, 1950), neutron diffraction (Levy & Peterson, 1952) and electron diffraction (Vainshtein, 1964) that in the room temperature form of ammonium chloride, phase II, the ammonium is not rotating. It is at random in two orientations. Thus these calculated values cannot be compared with the experimental.

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Chain structure of the orthorhombic modification of dicyclopentadienyl-lead containing bridging π-cyclopentadienyl rings.

By C. Panattoni, G. Bombieri and U. Croatto, *Centri Nazionali di Strutturistica Roentgenografica e Chimica delle Radiazioni e dei Radioelementi, Sezioni di Padova, Padova, Italy*

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Introduction

The structure of $Pb(C_5H_5)_2$ has aroused considerable interest. On the basis of infrared, nuclear magnetic resonance, ultraviolet spectra and dipole moment measurements Dave, Evans & Wilkinson (1959) concluded that the evidence supported the hypothesis of an angular sandwich structure. Previously, Fischer & Grubert (1956) suggested an angular 'σ-bonded structure' in accordance with their dipole moment measurements.

In view of criticism by Dave, Evans & Wilkinson (1959), Fritz & Fischer (1961) later extended their earlier measurements of the infrared spectra and concluded that there exists a 'predominantly π-bonding with some additional σ-bonding between metal atoms and rings in dicyclopentadienyltin and probably also in the lead compound'.

Experimental

We have prepared dicyclopentadienyl-lead by the Fischer & Grubert (1956) method. By sublimation in vacuum we have obtained two crystalline modifications which are very sensitive to exposure to air (Bombieri & Panattoni, 1966).

Modification 1 occurs as orthorhombic yellow needles, while modification 2, triclinic, has a prismatic habit of brown-yellow colour.

Very small crystals of modification 1 were enclosed in Lindemann capillaries in a nitrogen atmosphere. Multi-film Weissenberg methods with Cu $K\alpha$ radiation and precession techniques with Mo $K\alpha$ radiation were used to collect $hk0$ and $h0l$ intensity data, respectively. Intensities were measured with a photometer with a potentiometric recorder device and corrected for the Lorentz and polarization factors. On account of the uniform crystal cross-section and the very small dimensions of the crystal (less than 0·01 cm) absorption corrections were neglected. The unit cell containing four $Pb(C_5H_5)_2$ molecules has orthorhombic symmetry and possesses the following dimensions:

$$a = 16{\cdot}37 \pm 0{\cdot}04, \quad b = 6{\cdot}02 \pm 0{\cdot}03, \quad c = 9{\cdot}61 \pm 0{\cdot}03 \text{ Å}.$$

Observed density 2·361 g.cm^{-3}, calculated density 2·370 g.cm^{-3}. The observed systematic absences of $k+l \neq 2n$ for $\{0kl\}$ and $h \neq 2n$ for $\{h0l\}$ indicate as probable space groups $Pna2_1$ (C^{a}_{2v}) and $Pnam$ (D^{16}_{2h}).

The disposition of the lead atoms is consistent with both space groups.

If the space group is $Pnam$ the asymmetric unit contains only half a formula unit since there are only four $Pb(C_5H_5)_2$ per unit cell: the two cyclopentadienyl groups must be mirrored across the plane $z/c = 0{\cdot}25$ on which the crystallographically independent lead atom lies. Since the symmetry requirements of the non-centrosymmetric space group $Pna2_1$ do not specify the origin of the unit cell in the **c** lattice vector direction, the z/c coordinate of the independent lead atom can be arbitrarily chosen as 0·25.

From Patterson [001] and [010] projections, it was possible to determine the positions of the independent lead atom at $x/a = 0{\cdot}0821$, $y/b = 0{\cdot}1050$, $z/c = 0{\cdot}2500$. Two Fourier syntheses based on $Pnam$ were calculated with the signs given by the heavy atom. The coordinates of the maxima of electron density on the [010] map around the lead atom require a cyclopentadienyl ring across the symmetry plane $z/c = 0{\cdot}25$ with a second cyclopentadienyl ring positioned about the origin of the unit cell. Hence, the centrosymmetric space group $Pnam$ can be ruled out, since it contains a centre of symmetry at the origin, which would allow a cyclopentadienyl ring about it only if the structure were disordered. Since images of the cyclopentadienyl rings were generated phased on the centrosymmetrically located lead atoms, the non-centrosymmetric space group $Pna2_1$ was chosen as the correct one. Fig. 1 shows the positions of the cyclopentadienyl rings based on the interpretation of the Fourier maps.

The coordinates of the cyclopentadienyl rings were refined by the difference synthesis method. The unweighted reliability index for the $\{h0l\}$ and $\{hk0\}$ data decreased from 0·13 and 0·18 respectively to 0·08 and 0·10. With the use of anisotropic temperature coefficients for the lead atom and an identical isotropic factor for the carbon

Table 1. *Atomic coordinates and isotropic temperature factors*

	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$	$B(hk0)$	$B(h0l)$
Pb	0·0818+	0·0003	0·1030+	0·0007	0·2500+	0·0004	*	*
C(1)	0·4418+	0·004	0·4366+	0·004	0·0433+	0·004	1·50	3·46
C(2)	0·4968+	0·004	0·3000+	0·004	0·0267−	0·004	1·50	3·46
C(3)	0·5651+	0·004	0·3900+	0·002	0·0733−	0·004	1·50	3·46
C(4)	0·5484+	0·004	0·6300+	0·002	0·0267−	0·007	1·50	3·46
C(5)	0·4801+	0·003	0·6433+	0·002	0·0400+	0·006	1·50	3·46
C(6)	0·1900+	0·004	0·4233+	0·004	0·3533+	0·002	1·50	3·46
C(7)	0·1984+	0·004	0·4433+	0·004	0·2066+	0·002	1·50	3·46
C(8)	0·2334+	0·004	0·2466+	0·004	0·1400+	0·004	1·50	3·46
C(9)	0·2500+	0·002	0·1233+	0·003	0·2366+	0·005	1·50	3·46
C(10)	0·2217+	0·002	0·2000+	0·003	0·3600+	0·004	1·50	3·46

* For the lead atom the anisotropic thermal parameters are of the form $\exp\{-0{\cdot}25 \sum_{i=1}^{3} \sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\}$

$\{hk0\}$: $B_{11} = 2{\cdot}06$; $B_{12} = -0{\cdot}19$; $B_{22} = 3{\cdot}94$. $\{h0l\}$: $B_{11} = 3{\cdot}20$; $B_{13} = 0{\cdot}00$; $B_{33} = 4{\cdot}42$

Table 2. *Bond lengths*

Pb(1)–C(1)	3·041 Å	Pb(1)–C(6)	2·799 Å	C(1)–C(2)	1·392 Å	C(6)– C(7)	1·420 Å
Pb(1)–C(2)	3·055	Pb(1)–C(7)	2·830	C(2)–C(3)	1·320	C(7)—C(8)	1·462
Pb(1)–C(3)	3·116	Pb(1)–C(8)	2·832	C(3)–C(4)	1·536	C(8)—C(9)	1·218
Pb(1)–C(4)	3·053	Pb(1)–C(9)	2·761	C(4)–C(5)	1·291	C(9)—C(10)	1·354
Pb(1)–C(5)	3·006	Pb(1)–C(10)	2·589	C(5)–C(1)	1·393	C(10)–C(6)	1·442
Pb(2)–C(1)	3·014						
Pb(2)–C(2)	3·095	Average	2·762	Average C–C	1·386	Average C–C	1·379
Pb(2)–C(3)	3·210						
Pb(2)–C(4)	3·028	Pb(1)–Pb(2)	5·636				
Pb(2)–C(5)	2·973						
Average Pb–C	3·059						

atoms, the intensity data were further refined to final discrepancy values of 0·065 for $\{h0l\}$ and 0·064 for $\{hk0\}$.

Atomic form factors were calculated by the method of Vand, Eiland & Pepinski (1957) and the subsequent modifications of Forsyth & Wells (1959). The other crystallographic programs utilized in the structural analysis were written by Panattoni & Frasson (1962) for Olivetti Elea 6001 computers.

The accuracy of the proposed coordinates was calculated by the method of Cruickshank (1949). Standard deviations were calculated for the well-resolved atoms; no estimates were made for overlapping carbon atoms for which it was not possible to determine accurately the maximum of electron density. The final atomic coordinates with temperature factors are shown in Table 1. The observed and calculated structure factors are listed in Table 3. Table 2 gives the important bond lengths.

Table 3. *Observed and calculated structure factors* (× 10)

Unobserved reflexions for which $10F_o$ is listed as 0 have $10F_0 < 300$

$hk\bar{0}$

k	h	F_o	F_c
k=0	2	1570	1580
	4	439	351-
	6	2731	2776-
	8	1346	1412-
	10	827	742
	12	1594	1612
	14	1071	890
	16	0	218-
	18	899	890-
k=1	1	2537	2645
	2	1683	1736-
	3	710	701
	4	1128	1142-
	5	1783	1960-
	6	579	355-
	7	1672	1691-
	8	1324	1277
	9	0	245-
	10	1012	883
	11	1047	924
	12	0	150
	13	1121	1189
	14	766	735-
	15	0	118
	16	630	654-
	17	548	519-
k=2	0	696	593
	1	1232	1233-
	2	348	384
	3	1981	2202-
	4	736	610-
	5	1274	1341-
	6	653	547-
	7	1108	1105
	8	510	596-
	9	1430	1483
	10	0	211
	11	953	944
	12	0	293
	13	574	600-
	14	0	120
	15	1054	1154-
	16	0	37-
	17	600	616-
k=3	1	945	937-
	2	1555	1616-
	3	0	153-
	4	1391	1379-
	5	0	283
	6	0	82-
	7	725	569
	8	1123	1144
	9	0	13-
	10	1230	1252
	11	330	335-
	12	0	106-
	13	400	404-
	14	710	672-
	15	0	116-
	16	908	897-
k=4	0	1308	1424-
	1	0	148-
	2	925	797-
	3	940	831-
	4	537	490
	5	0	292-
	6	1143	1116
	7	635	413
	8	729	651
	9	514	434
	10	0	240-
	11	0	355
	12	851	767-
	13	0	268-
k=5	1	934	915-
	2	0	39
	3	0	111-
	4	0	256
	5	877	965
	6	0	33-
	7	788	833
	8	0	42
	9	0	239
	10	0	90-
	11	514	506-
k=6	0	600	627-
	1	0	292
	2	0	160-
	3	440	472
	4	0	235
	5	0	300
	6	504	528

$h\bar{0}l$

l	h	F_o	F_c	A_c	B_c
l=0	2	1684	1573	1573	0
	4	460	372	372-	0
	6	2429	2667	2667-	0
	8	1300	1313	1313-	0
	10	711	671	671	0
	12	1537	1382	1382	0
	14	702	716	716	0
	16	0	192	192-	0
	18	611	635	635-	0
l=1	2	2600	2816	2816-	9-
	4	1693	1872	1867-	144
	6	327	388	384-	58-
	8	[illegible]	1918	1918	53-
	10	1555	1469	1468	70-
	12	0	166	126	109-
	14	911	868	867-	48-
	16	783	802	800-	57-
	18	0	119	117-	24-
l=2	0	2538	2593	2589-	144-
	2	389	390	389-	39-
	4	1399	1307	1305	75
	6	2154	2427	2427	58-
	8	1105	1032	1022	145
	10	763	724	722-	52-
	12	1361	1311	1311-	23
	14	537	562	561-	44-
	16	0	313	313	16-
	18	711	705	705	26-
l=3	2	2405	2397	2397	42
	4	2344	2411	2411	68-
	6	303	294	294	10
	8	1323	1354	1354-	23-
	10	1470	1419	1418-	56-
	12	0	154	154-	17-
	14	656	688	686	58-
	16	712	740	740	35-
l=4	0	2495	2349	2345	142-
	2	1618	1490	1490	41
	4	906	836	835-	53-
	6	1674	1734	1733-	69
	8	958	819	819-	8
	10	478	491	491	10
	12	1034	1108	1108	23-
	14	470	507	507	23-
	16	0	198	194-	43-
l=5	2	1414	1293	1293-	31
	4	1447	1423	1418-	122-
	6	0	218	211	56
	8	1100	1077	1077	26-
	10	1115	1071	1071	7
	12	0	43	30	31
	14	598	614	612-	50-
	16	602	597	597-	2-
l=6	0	1428	1431	1424-	144
	2	982	794	785-	121-
	4	754	702	702	32
	6	1418	1358	1358	21
	8	673	628	623	80-
	10	0	321	317-	51
	12	812	832	831-	47-
l=7	2	986	1054	1061	85-
	4	920	1108	1105	92
	6	0	162	142	80-
	8	688	692	690-	54
	10	438	685	684-	44
l=8	0	825	973	970	85-
	2	324	358	349	81
	4	0	341	338-	49-
	6	716	835	834-	50-
	8	0	324	324-	8

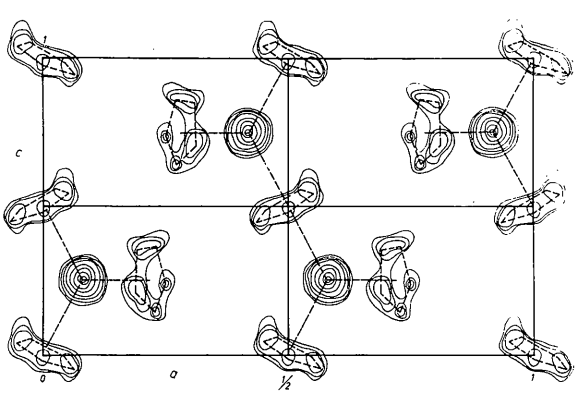

Fig. 1. Electron density projection on (010) for $Pb(C_5H_5)_2$. Contours at intervals of 2e.Å^{-3}. The levels for lead are arbitrary.

Discussion

Fig. 2 gives a perspective view of the molecules in the unit cell. One cyclopentadienyl ring is situated between two lead atoms with a mean lead–carbon distance of $3·06 \pm 0·1$ Å: the other cyclopentadienyl ring bonded to only one lead atom has a mean lead-carbon distance of $2·76 \pm 0·1$ Å. From the experimentally equivalent bond lengths in Table 3, it can be seen that the cyclopentadienyl rings are practically perpendicular to the axis Pb – (centre of the ring). The distance between the lead atoms in the chain is $5·636 \pm 0·001$ Å.

The angles between the centres A and B of the cyclopentadienyl rings and lead atom are A–Pb–$A_1 = 120°50'$ and A–Pb–$B = 118°20'$.

As found by Frasson, Menegus & Panattoni (1963) in $Tl(C_5H_5)$ and $In(C_5H_5)$, we have another example of a polymeric system involving cyclopentadienyl rings bridging non-transition-metal heavy atoms. The chains, oriented along the c axis, are realized with a zigzag disposition between the lead atoms and bridging cyclopentadienyl rings. This structure is in agreement with the hypothesis made for the monomer by Dave, Evans & Wilkinson (1959) in which they proposed that the lead atom is in an sp^2 hybridization state: two of the hybrid orbitals bind two cyclopentadienyl rings and the other is occupied by a lone pair of electrons. The chain polymerization can be considered to arise as a result of the interaction of this lone pair of electrons on a given lead atom of a monomeric molecule with the cyclopentadienyl ring of a neighbouring monomer.

A three-centre bond is obtained by overlapping two opposite sp^2 hybrid orbitals of two successive lead atoms in the chain and the σ-orbital (*i.e.* the molecular orbital of the π system belonging to the irreducible representation A_2'' of the D_{5h} symmetry group) of the cyclopentadienyl ring situated between them. In this way three molecular orbitals are produced: bonding, non-bonding and antibonding. The first two orbitals are doubly occupied. As a consequence the binding energy between a lead atom and a bridging cyclopentadienyl ring is smaller than in the free monomeric molecule.

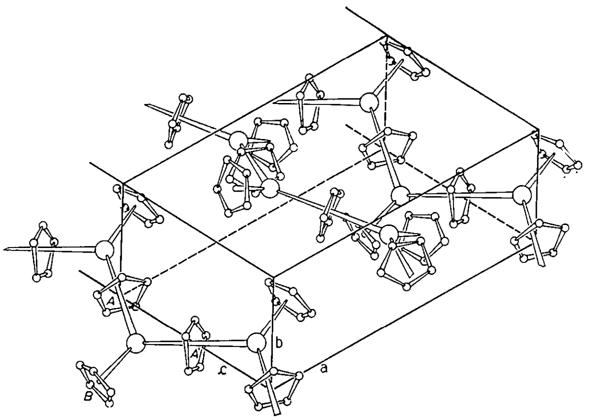

Fig. 2. A perspective view of the chains in $Pb(C_5H_5)_2$.

The p_z orbitals for the lead atoms and one of the e_1 orbitals of the cyclopentadienyl ring (with the right symmetry) are arranged in such a way as to give a conjugated system. A monomeric molecule participates in the π system with four electrons.

This configuration justifies a planar structure for the polymeric chain.

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Intensity corrections for the Guinier camera.

By W. H. Sas and P. M. de Wolff, *Laboratorium voor Technische Natuurkunde der Technische Hogeschool, Lorentzweg* 1, *Delft, The Netherlands*

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Intensity corrections for the Guinier camera

The integrated intensities as measured on a photometer record of powder diffraction lines on a Guinier film can be written as follows:

$$I = kpTF^2\mathrm{LP}ABSG;\ L = 1/\sin^2\theta\cos\theta \qquad (1)$$

where k, p, T, F, L and P are scale-, multiplicity-, temperature-, structure-, Lorentz- and polarization factor respectively. We shall show that the combined effect of the remaining factors A, B, S, G can be approximated by a linear function of $\cos(2\theta - \psi)$, ψ being the angle between specimen normal and crystal-reflected primary beam; and we present nomograms from which the normalized slope of this function can be found for $\psi = 30°$.

The factor A accounts for absorption in the specimen (thickness d, linear absorption coefficient μ):

$$A = \frac{1}{\mu d}\,\frac{\cos\psi\,.\,\cos\chi}{\cos\psi - \cos\chi}\,[\exp\{-(\mu d/\cos\psi)\} - \exp\{-(\mu d/\cos\chi)\}] \qquad (2)$$

where $\chi = |2\theta - \psi|$.

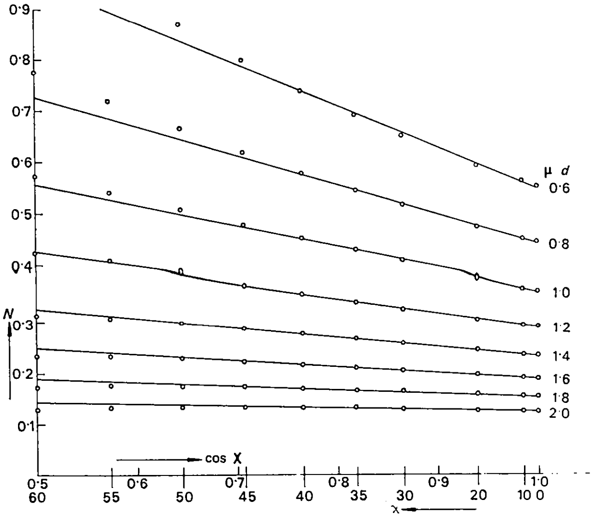

Fig. 1. The combined correction factor $N = ABSG$ (circles) as a function of $\cos\chi$ for $\psi = 30°$, $\mu_1 d_1 = \mu_2 d_2 = 0{\cdot}35$, $\mu_p d_p = 0{\cdot}1$ and 8 values of μd. The linear least-squares approximation is shown by the straight lines.

The factor B accounts for absorption in a layer which is often present in front of the film, *e.g.* wrapping paper or filter (thickness d_p, linear absorption coefficient μ_p).

$$B = \exp\{-(\mu_p d_p/\cos\chi)\}\,. \qquad (3)$$

S is the oblique incidence factor for integrated intensities:

$$S = \frac{[1 - \exp\{-(\mu_1 d_1/\cos\chi)\}]}{[1 - \exp\{-\mu_1 d_1\}]} \times \frac{[1 + \exp\{-(\mu_1 d_1 + \mu_2 d_2)/\cos\chi\}]}{[1 + \exp\{-(\mu_1 d_1 + \mu_2 d_2)\}]} \qquad (4)$$

where d_1 and d_2 are the thicknesses of one layer of emulsion and of the base, respectively and μ_1, μ_2 are the corresponding linear absorption coefficients (*International Tables for X-ray Crystallography*, 1962). G is a geometric factor:

$$G = 1/\cos\chi \qquad (5)$$

(*International Tables*, 1962), arising from the fact that the θ-dependent factor in (1) is valid for a constant specimen–film distance, whereas in the Guinier camera that distance varies as $\cos\chi$. Since a photometer measures the energy over a constant height of the diffraction line, the corresponding fraction of the total energy in the Debye–Scherrer cone contains the extra factor $1/\cos\chi$.*

If we define $N = ABSG$, then N is a function of $\cos\chi$, with parameters ψ, μd, $\mu_1 d_1$, $\mu_2 d_2$, $\mu_p d_p$, because A, B, S, G are all functions of $\cos\chi$. For $\mu_1 d_1 = \mu_2 d_2$ as well as for $\mu_2 d_2 = 0$ and a great number of different combinations of

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* Hellner (1954) gave an entirely different expression for the geometric factor, which has been cited and tabulated by Sagel (1958). Professor Hellner (private communication) now states that his formula resulted from an erroneous derivation and kindly pointed out to us that the correct expression was given first by Hägg & Regnström (1944).