The nitrogen atom of the NH_2 group forms two H-bonds (N(1)...O(2) (x, y, 1+z) 3.09 and N(1)...O(1) (1−x, −1+y, 1−z) 3.10 Å), which join the layers into a three-dimensional polymeric structure (see Fig. 1).

The sum of the angles of the N(2) nitrogen atom, 359.9°, shows that it has trigonal sp^2 hybridization.

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CRYSTAL AND MOLECULAR STRUCTURE OF MONOAQUO-BIS-(p-HYDROXYBENZOATO)LEAD(II) MONOHYDRATE

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An x-ray structural study of monoaquo-bis-(p-hydroxybenzoato)lead(II) monohydrate $[Pb(p\text{-}HOC_6H_4COO)_2(H_2O)]\cdot H_2O$ has been carried out (diffractometer, λMoK_α, 1915 reflections, heavy-atom method, anisotropic refinement, R = 0.098). The crystals are monoclinic, $a = 18.735(9)$, $b = 7.464(3)$, $c = 11.650(4)$ Å, $\beta = 113.116(30)°$, $V = 1498.31$ Å^3, $d_{calc} = 2.15$ g/cm^3, $Z = 4$, space group $P2_1/c$. The carboxyl group of one organic ligand forms a chelate ring with the Pb atom (Pb−O, 2.39(4), 2.52(5) Å), and each O atom acts as a bridge between neighboring metal atoms related by 2_1 and $\bar{1}$ symmetry (Pb−O 2.83(5), 2.89(3) Å). The carboxyl group of the second ligand acts as a bridge through one O atom joining two neighboring Pb atoms (Pb−O 2.50(2), 2.65(3) Å). The other O atom of this group is not coordinated to a metal, but forms an H-bond with two water molecules (O...O 2.83(5), 2.82(5) Å). The coordination of Pb is brought up to 8 by two water molecules (Pb−OH_2 2.61(14), 2.70(3) Å). The OH groups of the ligand are not coordinated to Pb, but take part in H-bonding.

The present work was carried out as part of a study of the complexes of divalent lead with benzoic acid and its derivatives [1-3] and describes a study of the structure of the complex with p-hydroxybenzoic acid (PHBA).

EXPERIMENTAL, STRUCTURE DETERMINATION, AND REFINEMENT

Hot aqueous solutions of Pb^{2+} acetate and PHBA (1 : 2) were mixed, boiled until the odor of the acetic acid disappeared, and filtered. At room temperature the filtrate gave glistening white crystals with the composition $Pb(p\text{-}HOC_6H_4COO)_2\cdot 2H_2O$ (I).

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TABLE 1. Coordinates of the Atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
Pb	5190(1)	244(2)	3248(1)	C(4)	1836(29)	—902(51)	3516(38)
O(1)	606(20)	1714(39)	334(32)	C(5)	1357(20)	—1851(44)	2460(37)
O(2)	3759(18)	0555(36)	—341(29)	C(6)	1669(26)	—2655(53)	1684(43)
O(3)	4194(16)	2005(30)	1544(26)	C(7)	2451(20)	—2484(54)	1913(34)
O(4)	4125(26)	—1822(36)	2592(37)	C(8)	3689(27)	1295(37)	507(31)
O(5)	4153(16)	—153(36)	4106(23)	C(9)	2854(25)	1458(41)	451(38)
O(6)	582(22)	—2062(35)	2146(28)	C(10)	2714(27)	2381(47)	1416(38)
O(7)	87(22)	—0630(40)	3734(28)	C(11)	1972(34)	2487(56)	1356(40)
O(8)	4943(15)	3783(25)	3858(22)	C(12)	1323(26)	1654(48)	353(34)
C(1)	3740(28)	—1159(46)	3174(28)	C(13)	1469(20)	783(48)	—613(33)
C(2)	2935(20)	—1517(43)	3040(37)	C(14)	2247(27)	684(50)	—560(41)
C(3)	2607(22)	—742(48)	3723(31)				

TABLE 2. Bond Lengths, d, Å

Bond	d	Bond	d
Pb—O(3)	2,50(3)	C(2)—C(3)	1,31(6)
Pb—O(3)*	2,65(4)	C(3)—C(4)	1,37(7)
Pb—O(4)	2,39(4)	C(4)—C(5)	1,39(5)
Pb—O(4)*	2,89(3)	C(5)—C(6)	1,38(7)
Pb—O(5)	2,52(5)	C(6)—C(7)	1,39(7)
Pb—O(5)*	2,83(5)	C(7)—C(2)	1,43(5)
Pb—O(8)	2,61(4)	Average	1,38
Pb—O(8)*	2,70(3)	C(9)—C(10)	1,42(6)
O(1)—C(12)	1,33(6)	C(10)—C(11)	1,36(8)
O(6)—C(5)	1,36(5)	C(11)—C(12)	1,45(5)
O(2)—C(8)	1,18(5)	C(12)—C(13)	1,42(6)
O(3)—C(8)	1,32(4)	C(13)—C(14)	1,43(8)
O(4)—C(1)	1,26(7)	C(14)—C(9)	1,40(5)
O(5)—C(1)	1,29(4)	Average	1,41
C(1)—C(2)	1,48(6)	O(2)—O(8)†	2,8[illegible]‡
C(8)—C(9)	1,54(7)	O(6)—O(7)	2,60(6)‡
O(1)—O(6)*	2,88(5)‡	O(6)—O(7)†	2,95(5)‡
O(1)—O(7)*	2,81(4)‡		
O(2)—O(8)*	2,82(5)‡		

*O(3): 1−x, y−1/2, 1/2−z; O(4): 1−x, 1/2+y, 1/2−z; O(5): 1−x, −y, 1−z; O(8): 1−x, y−1/2, 1/2−z; O(6): −x, −y, −z; O(7): −x, 1/2+y, 1/2−z.

†O(7): −x, y−1/2, 1/2−z; O(8): x, 1/2−y, z−1/2.

‡ Hydrogen bonds.

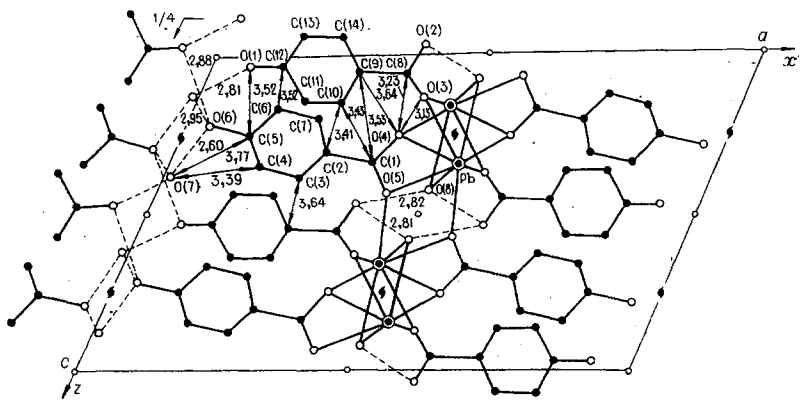

Fig. 1. Projection of the structure on the (001) plane.

TABLE 3. Valence Angles ω, deg

Angle	ω	Angle	ω
O(3)PbO(4)	79,43(3)	O(4)*PbO(5)*	108,94(4)
O(3)PbO(5)	85,73(3)	O(4)*PbO(8)*	87,49(3)
O(3)PbO(8)	64,68(3)	O(5)*PbO(8)*	145,05(4)
O(3)PbO(3)*	135,69(3)	O(6)*O(1)C(12)	113,28
O(3)PbO(4)*	68,01(3)	O(6)O(1)O(7)*	91,81
O(3)PbO(5)*	138,27(4)	C(12)O(1)O(7)*	129,15
O(3)PbO(8)*	76,17(3)	O(8)*O(2)O(8)†	75,02(3)
O(4)PbO(5)	51,52(3)	O(8)*O(2)C(8)*	95,50(3)
O(4)PbO(8)	117,90(4)	C(8)O(2)O(8)†	121,17(4)
O(4)PbO(3)*	73,75(3)	PbO(3)Pb*	104,17(4)
O(4)PbO(4)*	143,38(4)	PbO(3)C(8)	124,06(4)
O(4)PbO(5)*	106,43(3)	C(8)O(3)Pb*	125,51(4)
O(4)PbO(8)*	68,27(3)	C(1)O(4)Pb	98,94(3)
O(5)PbO(8)	75,82(3)	C(1)O(4)Pb*	158,65(4)
O(5)PbO(3)*	103,40(4)	PbO(4)Pb *	99,81(3)
O(5)PbO(4)*	137,21(4)	PbO(5)Pb†	111,08(3)
O(5)PbO(5)*	68,92(3)	PbO(5)C(1)	92,03(4)
O(5)PbO(8)*	68,27(3)	C(1)O(1)Pb†	139,28(4)
O(8)PbO(3)*	159,60(5)	O(1)*O(6)O(7)*	71,20(4)
O(8)PbO(4)*	62,70(3)	O(1)*O(6)C(5)	125,55(4)
O(8)PbO(5)*	76,94(3)	O(1)*O(6)O(7)	108,96(3)
O(8)PbO(8)*	137,73(4)	O(7)O(6)O(7)*	113,35(3)
O(3)*PbO(4)*	119,09(4)	O(7)O(5)O(5)	113,70(4)
O(3)*Pb(O(5)*	83,75(3)	C(5)O(6)O(7)*	117,45(3)
O(3)*PbO(8)*	61,41(3)	O(1)**O(7)O(6)†	124,97(4)
O(6)O(7)O(1)†	109,4(5)	C(5)C(6)C(7)	120,9(4)
O(6)O(7)O(6)†	110,1(4)	C(6)C(7)C(2)	116,9(3)
PbO(8)Pb*	99,5(4)		
PbO(8)O(2)*	124,9(4)	O(3)C(8)O(2)	123,6(5)
PbO(8)O(2)†	118,0(5)	O(3)C(8)C(9)	110,9(4)
O(2)*O(8)O(2)†	104,9(3)	O(2)C(8)C(9)	116,3(3)
O(2)† O(8)Pb*	92,2(3)	Σ	360,9
O(2)*O(8)Pb*	111,8(4)	C(8)C(9)C(10)	120,0(3)
		C(8)C(9)C(14)	118,5(4)
O(4)C(1)O(5)	113,3(4)	C(10)C(9)C(14)	121,4(4)
O(4)C(1)C(2)	130,0(3)	Σ	360
O(5)C(1)C(2)	116,1(4)	C(9)C(10)C(11)	119,0(3)
Σ	359,6	C(10)C(11)C(12)	126,9(5)
C(1)C(2)C(7)	115,5(4)		
C(1)C(2)C(3)	123,7(4)	C(11)C(12)C(13)	118,2(5)
C(3)C(2)C(7)	119,3(4)	C(11)C(12)O(1)	121,1(4)
Σ	358,6	O(1)C(12)C(13)	120,6(3)
C(2)C(3)C(4)	124,3(3)	Σ	360,0
C(3)C(4)C(5)	117,7(4)	C(12)C(13)C(14)	119,9(3)
C(4)C(5)C(6)	120,4(4)	C(13)C(14)C(9)	119,3(4)
C(4)C(5)O(6)	122,9(4)		
O(6)C(5)C(6)	116,6(3)		
Σ	359,9		

*Pb: $1-x$, $1/2+y$, $1/2-z$, O(1): $-x$, $-y$, $-z$, O(2): x, $1/2-y$, $1/2+z$, O(3): $1-x$, $y-1/2$, $1/2-z$, O(4): $1-x$, $1/2+y$, $1/2-z$, O(5): $1-x$, $-y$, $1-z$, O(6): $-x$, $-y$, $-z$, O(7): $-x$, $1/2+y$, $1/2-z$, O(8): $1-x$, $y-1/2$, $1/2-z$.
†Pb: $1-x$, $-y$, $1-z$, O(2): $1-x$, $1/2+y$, $1/2-z$, O(6): $-x$, $1/2+y$, $1/2-z$, O(7): $-x$, $y-1/2$, $1/2-z$, O(8): x, $1/2-y$, $z-1/2$; O(1): $-x$, $1/2+y$, $1/2-z$.

The x-ray diffraction study was carried out on a "Syntex $P2_1$" automatic diffractometer (λMoKα, graphite monochromator, $\theta/2\theta$ scanning by the method of ordinate analysis, $2\theta \leq 50°$). The crystals are monoclinic, $a = 18.735(9)$, $b = 7.464(3)$, $c = 11.650(4)$ Å, $\beta = 113.116(30)°$, $Z = 4$, $V = 1498.31$ Å^3, $M = 485.35$, $d_{calc} = 2.15$ g/cm^3, space group $P2_1/c$.

The intensities of 2051 independent reflections were measured. 1915 reflections with $I \geq 2\sigma$ were used in the structure calculations.*

*All the calculations were carried out on a BÉSM-6 computer using the programs "Rentgen-75" [4].

The coordinates of the lead atom were determined from the three-dimensional Patterson function. Two Fourier syntheses were required to locate all the atoms other than hydrogen. The refinement was carried out by the method of least squares in the anisotropic approximation. The final value of R = 0.098. The coordinates of the basis atoms are given in Table 1.*

DESCRIPTION OF THE STRUCTURE

The crystal structure of compound I consists of a three-dimensional polymer. Against the background of the overall structure, however, it is possible to distinguish a compact chain of Pb atoms, which are joined to one another by the oxygen atoms of the COO^- group of PHBA and the molecules of coordinated water. This chain can be clearly distinguished in the projection of the structure (010) along the line [1/2 z] (see Fig. 1).

The bond lengths and valence angles are given in Tables 2 and 3.

The carboxyl group of one of the PHBA ligands forms a chelate ring with a metal atom (Pb–O(4) 2.39(4), Pb–O(5) 2.52(5) Å), and simultaneously its oxygen atoms form a bridge between neighboring lead atoms, related by 2_1 and $\bar{1}$ symmetry: Pb(1–x, 1/2–y, 1/2–z)–O(4) 2.89(3), Pb(1–x, –y, 1–z)–O(5) 2.83(5) Å. The O(3) atom of the carboxyl group of the second PHBA anion acts as a bridge joining lead atoms related by symmetry (Pb–O(3), 2.50(3), Pb(1–x, 1/2+y, 1/2–z) –O(3) 2.65(4) Å), and the O(2) atom of the same group forms a H-bond with two molecules of coordinated water (O(2)...H–O(8) (1–x, y – 1/2, 1–z) 2.82(5), O(1)...H–O(8) (x, 1/2–y, z–1/2) 2.83(5) Å, see Table 2).

The coordination number of the central atom of the complex is brought up to 8 by two water molecules (Pb–O(8) 2.61(4), Pb–O(8) (1–x, y–1/2, 1–z) 2.70(3) Å).

Thus the oxygen atoms of the carboxyl groups and water molecules join the complexes to form a two-dimensional polymeric layer parallel to (100). The sum of the internal angles of the quadrilateral PbO(4)C(1)-O(5) is 355.9°, which within the limits of error corresponds to the ideal value of 360° and indicates that the chelate ring is planar. The benzene rings are planar, and the carboxyl and hydroxyl groups are in the same plane as the ring. The C–O distances in the carboxyl groups, except for the distance C(8)–O(2) 1.18(5) Å, and also the average C–C distances in the benzene rings, 1.39 and 1.42 Å, show good agreement with the corresponding values in the structures studied earlier [1, 2]. short, the C(8)–O(2) distance corresponds to a double bond and agrees with published data [5] within the limits of error. The OH groups of the ligand are not in the coordination sphere of the metal. They form H-bonds with the molecule of water of crystallization and with one another (see Table 2): O(1)...H–O(7) (–x, 1/2+y, 1/2–z) 2.81(4), O(1)...H–O(6) (–x, –y, –z) 2.88(9), O(6)...H–O(7) 2.60(6), O(6)...H–O(7) (–x, y–1/2, 1/2–z) 2.95(5) Å.

Thus the two-dimensional polymeric layers are "cross-linked" to form a three-dimensional polymeric structure. The other intermolecular distances have the usual van der Waals values. The volume corresponding to one chemical bond, calculated by the published method [6], is 9.1 $Å^3$.

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*The Table of anisotropic temperature factors can be obtained from the authors.