5. K. N. Semenenko, G. N. Boiko, A. P. Borisov, and V. D. Makhaev, Proceedings of the Third All-Union Conference on the Chemistry and Technology of Molybdenum and Tungsten, Ordzhonikidze, 1977 [in Russian], p. 33.
6. E. B. Lobkovskii, K. N. Semenenko, A. P. Borisov, and V. D. Makhaev, Zh. Strukt. Khim. (in press).
7. J. L. Hoard and J. V. Silverton, Inorg. Chem., 2, 235 (1963).
8. C. A. Tolman, Chem. Rev., 313 (1977).

AN X-RAY STRUCTURAL STUDY OF COMPLEXES OF p-AMINOBENZOIC ACID WITH METALS.

V.* CRYSTAL AND MOLECULAR STRUCTURE OF BIS(p-AMINOBENZOATO)LEAD(II)

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Bis(p-aminobenzoato)lead(II) $[Pb(H_2NC_6H_4COO)_2]_n$ has been studied by x-ray diffraction (diffractometer, λMoK_α, 2429 reflections, heavy atom method, anisotropic refinement, R = 0.081). The crystals are monoclinic, a = 8.766(4), b = 7.505(4), c = 22.758(18) Å, β = 97.16(5)°, Z = 4, space group $P2_1/c$. The coordination number of the metal atom is 6. The carboxyl groups form chelate rings with the lead atom (Pb—O 2.37-2.52 Å). One of the groups acts as a bridge joining two other lead atoms (Pb—O 2.67 and 2.84 Å). The nitrogen atoms are not in the coordination sphere of the metal atom.

The present work was carried out as part of a program for studying the structures of the complexes of p-aminobenzoic acid (PABA) with metals [2]. The possible interactions of lead with metabolites, the importance of which for life processes has been the subject of discussion in many papers [3-6], and in particular with PABA are of undoubted interest for inorganic biochemistry. Although some papers have been devoted to the structure of individual lead complexes [7-16], their number is not large. In particular, there are no systematic studies of the structures of lead carboxylates.

The present paper describes an x-ray structural study of the complex of p-aminobenzoic acid with divalent lead.

EXPERIMENTAL, INTERPRETATION AND REFINEMENT OF THE STRUCTURE

The complex studied was obtained by the reaction of PABA with lead acetate; 1.186 g of $Pb(CH_3CO_2)_2$ was dissolved in 0.5 liter of water (several drops of acetic acid were added to the solution to prevent the hydrolysis of lead acetate), and the solution was heated in a flask of one liter capacity, 1 g of PABA was added gradually, and the mixture was boiled until the odor of acetic acid disappeared. The solution was then filtered and left to crystallize at room temperature. After several days, crystals with a yellowish tinge separated.

The x-ray diffraction study was carried out on a "Syntex $P2_1$" automatic diffractometer controlled by a "Novo-1200" minicomputer using the programs of the "XTL Syntex" system (λMoK_α, graphite monochromator, $\theta/2\theta$-scanning, $2\theta \leqslant 55°$). The crystals are monoclinic: a = 8.766(4), b = 7.505(4), c = 22.758(18) Å, β = 97.16(5)°, V = 1485.5 Å^3, M = 479.47, d_{calc} = 2.14 g/cm^3, Z = $4Pb(H_2NC_6H_4COO)_2$, space group $P2_1/c$.

*For Paper IV, see [1].

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TABLE 1. Coordinates of the Atoms ($\times 10^5$)

Atoms	x	y	z	Atoms	x	y	z
Pb	109696(13)	42765(14)	28672(5)	C(5)	30737(342)	43306(472)	16152(128)
O(1)	87686(173)	57649(292)	22338(82)	C(6)	40066(334)	58001(422)	14989(132)
O(2)	86697(218)	29258(251)	24196(97)	C(7)	55907(339)	57971(417)	16551(134)
O(3)	95167(253)	55911(308)	35814(86)	C(8)	94756(360)	42114(533)	39074(137)
O(4)	100962(274)	28431(274)	37680(98)	C(9)	85973(369)	42916(520)	44352(127)
N(1)	15025(222)	44140(386)	14805(121)	C(10)	78622(399)	58992(580)	45700(137)
N(2)	63200(420)	45982(532)	59572(124)	C(11)	70577(401)	59687(602)	50786(142)
C(1)	79849(258)	42710(378)	22052(116)	C(12)	70640(408)	44874(625)	54419(145)
C(2)	62064(273)	42620(446)	19615(119)	C(13)	78151(546)	29001(545)	53020(165)
C(3)	53761(302)	27659(378)	20561(134)	C(14)	85927(444)	27903(498)	48000(153)
C(4)	38176(351)	28077(391)	18797(134)				

TABLE 2. Bond Lengths d, Å

Bond	d	Bond	d
Pb—O(1)	2,521(18)	C(4)—C(5)	1,413(45)
Pb—O(1)*	2,658(22)	C(5)—C(6)	1,417(33)
Pb—O(2)	2,370(20)	C(6)—C(7)	1,390(42)
Pb—O(2)†	2,842(19)	C(7)—C(2)	1,418(31)
Pb—O(3)	2,399(21)	Average	1,397
Pb—O(4)	2,519(22)		
O(1)—C(1)	1,312(27)	C(8)—C(9)	1,507(44)
O(2)—C(1)	1,243(33)		
O(3)—C(8)	1,277(43)	C(9)—C(10)	1,419(55)
O(4)—C(8)	1,222(43)	C(10)—C(11)	1,429(47)
N(1)—C(5)	1,375(36)	C(11)—C(12)	1,385(59)
N(2)—C(12)	1,414(46)	C(12)—C(13)	1,416(61)
C(1)—C(2)	1,588(34)	C(13)—C(14)	1,404(55)
		C(14)—C(9)	1,400(51)
C(2)—C(3)	1,370(42)	Average	1,409
C(3)—C(4)	1,375(41)		

*2 − x, y − 1/2, 1/2 − z.
†2 − x, 1/2 + y, 1/2 − z.

TABLE 3. Valence Angles ω, deg

Angle	ω	Angle	ω
O(1)PbO(1)*	117,3(6)	C(3)C(2)C(7)	124,5(27)
O(1)PbO(2)	52,7(7)	C(2)C(3)C(4)	117,6(27)
O(1)PbO(2)†	62,7(6)	C(3)C(4)C(5)	122,1(28)
O(1)PbO(3)	76,8(7)	C(4)C(5)C(6)	117,6(28)
O(1)PbO(4)	111,5(7)	C(5)C(6)C(7)	122,2(28)
O(1)*PbO(2)	67,5(6)	C(6)C(7)C(2)	115,7(27)
O(1)*PbO(2)†	157,3(6)	Average	120
O(1)*PbO(3)	121,7(7)		
O(1)*PbO(4)	71,6(7)	N(1)C(5)C(4)	121,9(28)
O(2)PbO(2)†	115,2(6)	N(1)C(5)C(6)	120,6(28)
O(2)PbO(3)	88,4(7)	O(3)C(8)O(4)	119,0(31)
O(2)PbO(4)	80,7(7)	O(3)C(8)C(9)	119,0(30)
O(2)† PbO(3)	81,0(7)	O(4)C(8)C(9)	121,9(31)
O(2)† PbO(4)	130,7(7)	C(8)C(9)C(10)	119,8(30)
O(3)PbO(4)	51,9(7)	C(8)C(9)C(14)	118,7(31)
PbO(1)Pb†	114,9(7)		
PbO(1)C(1)	153,3(17)	C(10)C(9)C(14)	121,4(32)
Pb† O(1)C(1)	90,5(15)	C(9)C(10)C(11)	119,3(33)
PbO(2)Pb*	113,4(7)	C(10)C(11)C(12)	119,2(35)
PbO(2)C(1)	139,0(17)	C(11)C(12)C(13)	120,6(36)
Pb * O(2)C(1)	99,5(16)	C(12)C(13)C(14)	121,3(37)
PbO(3)C(8)	96,7(19)	C(13)C(14)C(9)	118,2(34)
PbO(4)C(8)	92,5(20)	Average	120
O(1)C(1)O(2)	116,8(23)		
O(1)C(1)C(2)	120,4(22)	N(2)C(12)C(11)	118,7(35)
O(2)C(1)C(2)	122,6(23)	N(2)C(12)C(13)	120,8(35)
C(1)C(2)C(3)	117,8(24)		
C(1)C(2)C(7)	117,7(24)		

*2 − x, y − 1/2, 1/2 − z.
†2 − x, 1/2 − y, 1/2 − z.

TABLE 4. Coefficients of the Equations of the Planes Ax + By + Cz = D of Various Planar Fragments of the Complex and the Angles between the Individual Planes (absolute coordinates)

Plane	Atoms and their deviations from the planes in Å							A	B	C	D	Angle with the planes in degrees		
												I	II	III
I	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	0,28	−0,38	−0,88	−3,77			81,6
	−0,06	0,01	0,04	0,01	−0,06	−0,01	0,06							
	Pb *	O(1)*	O(2) *	O(3)*	O(4)*	N(1)*	C(8)*							
	−1,08	−0,35	0,05	0,38	1,41	−0,19	1,46							
II	O(1)	O(2)	C(1)	Pb *	O(3)*	O(4)*	N(1)*	0,42	−0,20	−0,89	−2,40	12,9		
	0	0	0	−0,22	1,62	2,22	−0,86							
	C(2)*	C(3)*	C(4)*	C(5)*	C(6)*	C(7)*								
	−0,13	−0,41	−0,61	−0,56	−0,19	0,06								
III	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)	−0,77	0,32	−0,55	−6,07		84,3	
	0,01	−0,02	0	−0,01	0,01	0	−0,01							
	Pb *	O(1)*	O(2)*	O(3)*	O(4)*	N(2)*	C(1)*							
	−0,02	−0,78	−1,58	0,04	−0,03	0,07	−0,57							
IV	0(3)	O(4)	C(8)	Pb *	O(1)*	O(2)*	N(2)*	−0,79	0,29	−0,54	−6,42	81,6	84,8	2,2
	0	0	0	0,02	−0,65	−1,38	−0,07							
	C(1)*	C(2)*	C(9)*	C(10)*	C(11)*	C(12)*	C(13)*							
	−0,40	1,07	−0,07	−0,1	−0,14	−0,09	−0,05							

*Atoms not included in the calculation of the equation of the corresponding plane.

TABLE 5. Short Intermolecular Distances d ⩽ 3.8 Å

Atoms	d	Atoms	d
Pb ... N(1) (I'')	3,249	O(4) ... C(12) (IV)	3,510
Pb ... N(2) (IV)	3,452	N(1) ... C(1) (I')	3,675
Pb ... C(4) (I'')	3,728	N(1) ... C(8) (III')	3,780
Pb ... C(5) (I'')	3,582	N(1) ... C(10) (II)	3,649
O(1) ... N(1) (I'')	3,276	N(2) ... C(2) (V)	3,705
O(1) ... C(4) (III')	3,564	N(2) ... C(3) (V)	3,260
O(1) ... O(2) (III)	2,803	N(2) ... C(4) (V)	3,695
O(1) ... O(4) (III)	3,033	N(2) ... C(8) (IV)	3,766
O(2) ... O(3) (III)	3,419	C(2) ... C(4) (III')	3,748
O(2) ... N(1) (I'')	3,647	C(3) ... C(6) (II)	3,583
O(2) ... N(1) (II)	3,651	C(3) ... C(7) (II)	3,482
O(2) ... N(1) (III')	3,003	C(4) ... C(7) (II)	3,638
O(3) ... N(2) (IV)	3,673	C(4) ... C(10) (II)	3,727
O(3) ... C(1) (III)	3,398	C(5) ... C(10) (II)	3,745
O(3) ... C(4) (III')	3,413	C(8) ... C(11) (IV)	3,582
O(3) ... C(5) (III')	3,602	C(8) ... C(12) (IV)	3,351
O(3) ... C(12) (IV)	3,503	C(8) ... C(13) (IV)	3,537
O(3) ... C(13) (IV)	3,425	C(9) ... C(10) (IV)	3,609
O(4) ... N(1) (I'')	2,951	C(9) ... C(13) (IV)	3,771
O(4) ... N(2) (IV)	3,664	C(9) ... C(14) (IV)	3,581
O(4) ... C(11) (IV)	3,502	C(10) ... C(14) (IV)	3,401

*The Arabic numerals give the numbers of the atoms of the molecules in accordance with Table 1, and the Roman numerals give the numbers of the molecules in accordance with Fig. 1; original molecule I at x, y, z; I' at 1 − x, y, z; I'' at 1 + x, y, z; II at 1 − x, y − 1/2, 1/2 − z; III at 2 − x, 1/2 + y, 1/2 − z; III' at 1 − x, 1/2 + y, 1/2 − z; IV at 1 − x, 1 − y, 1 − z; and V at 1 − x, 1/2 − y, 1/2 + z.

The intensities of 2696 independent reflections were measured. 2429 reflections with $F^2 \geqslant 2\sigma$ were used in the structural calculations.

The structure was determined by the heavy atom method. The coordinates of the lead atom were determined from the three-dimensional Patterson function. The divergence factor R amounted to 0.16 after two cycles of the refinement in the anisotropic approximation. Two Fourier syntheses were required to detect 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 was 0.081. The positional parameters are given in Table 1.*

DESCRIPTION OF THE STRUCTURE

The crystal structure of the complex is made up of one-dimensional polymer chains parallel to the b axis (see Fig. 1). The bond lengths and valence angles are given in Tables 2 and 3. Table 4 gives the equations of the planes of the phenyl rings and the planes of the other planar fragments of the molecule, the deviations of the atoms from the corresponding planes, and the angles between the individual planes.

The carboxyl group of one of the crystallographically nonequivalent PABA anions forms a chelate ring with the metal atom (Pb—O 2.521(18) and 2.370(20) Å) and simultaneously acts as a bridge joining two other neighboring Pb atoms (Pb—O 2.658(22) and 2.842(19) Å). The second PABA anion forms a chelate ring with only one Pb atom. The average value of the bond length Pb—O is 2.552 Å. The lengths of the bonds Pb—O in the structure agree with the analogous distances 2.71 Å in $2PbCO_3 \cdot Pb(OH)_2$ [7], 2.81 Å in $Pb(NO_3)_2$ [8], 2.37-3.01 Å in $Pb[SC(NH_2)_2] \cdot (C_2H_3O_2)_2$ [9], 2.47-2.96 Å in $Pb(C_6H_4NO_2)_2 \cdot H_2O$ [11], 2.59-2.94 Å in $Pb(HCOO)_2 \cdot [SC(NH_2)_2]_2 \cdot H_2O$ [12], 2.44 Å in $Pb[OP(C_6H_5)_2O]_2$ [14], 2.56-2.87 Å in $C_{15}N_9H_9Pb_2(NO_3)_4 \cdot 2H_2O$ [15], and 2.43-2.51 Å in $(C_6H_5)_3PbOC_6H_3(F)NO_2$ [16]. Thus the coordination number of the Pb(II) atom in the structure studied is 6. The coordination polyhedron is considerably deformed, and its shape is close to that of a trigonal prism.

The sum of the internal angles in the chelate ring PbO(1)C(1)O(2) is 461.8°, and that in the chelate ring PbO(3)C(8)O(4) is 360.1°, that is, the sum for the first ring differs considerably from the ideal value of 360°. This indicates that this chelate ring has a non-

*The values of the anisotropic thermal parameters can be obtained from the authors.

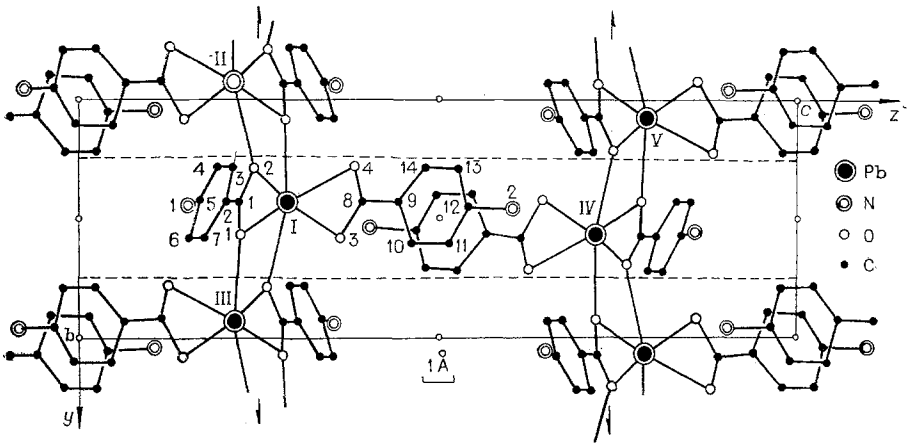

Fig. 1. Crystal structure of the complex (projection along [100]).

planar structure. The N atoms of the amino groups of PABA are not in the coordination sphere of the Pb atom. The distance 2.95(3) Å between the nitrogen atom and the nearest oxygen atom from the COO^- group of another chain is sufficient for hydrogen bond formation.

Tables 2-4 show that, within the limits of experimental error, the benzene rings are planar, with the usual bond lengths and valence angles.

Table 5 gives the short intermolecular distances, and Fig. 1 gives the crystal structure of the complex. The volume corresponding to the chemical bond [17] is 9.8 $Å^3$.

LITERATURE CITED

1. I. R. Amiraslanov, Kh. S. Mamedov, E. M. Movsumov, F. N. Musaev, and G. N. Nadzhafov, Zh. Strukt. Khim., 20, 1075 (1979).
2. I. R. Amiraslanov, Kh. S. Mamedov, and E. M. Movsumov, Summaries of Papers Presented at the First All-Union Conference on Inorganic Crystal Chemistry, Zvenigorod, 1977 [in Russian], p. 53.
3. J. S. Thayer, J. Organometal. Chem., 76, 265 (1974).
4. G. Vivoli, Tech. Sanit., 12, 467 (1974).
5. G. F. Okeanova, Nauch. Trudy Kubansk. Med. Inst., 46, 67 (1975).
6. D. Cotrone, Ig. Sanita Pubbl., 32, 3 (1976).
7. J. M. Cowley, Acta Crystallogr., 9, 391 (1956).
8. W. C. Hamilton, Acta Crystallogr., 10, 103 (1957).
9. M. Nardelli, G. Fava, and G. Branehi, Acta Crystallogr., 13, 898 (1960).
10. T. Ito, Acta Crystallogr., B28, 1034 (1972).
11. C. M. Biagini, M. A. Gaetani, C. Guastini, and M. Nardelli, Gazz. Chim. Ital., 102, 1034 (1972).
12. I. Goldberg and F. H. Herbstein, Acta Crystallogr., B29, 246 (1973).
13. C. M. Biagini, M. A. Gaetani, C. Guastini, and A. Musatti, Gazz. Chim. Ital., 105, 117 (1975).
14. P. Colamarino, P. L. Orioli, W. D. Baenzinger, and H. D. Gillman, Inorg. Chem., 15, 800 (1976).
15. E. I. Lerner and S. J. Lippard, Inorg. Chem., 16, 1537 (1977).
16. N. G. Bokii, A. I. Udel'nov, Yu. T. Struchkov, D. N. Kravtsov, and V. M. Pachevskaya, Zh. Strukt. Khim., 18, 1025 (1977).
17. Kh. S. Mamedov and E. M. Movsumov, Azerb. Khim. Zh., 2, 83 (1976).