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

VI.* THE CRYSTALS AND MOLECULAR STRUCTURE OF NITRATO-(p-AMINOBENZOATO)LEAD(II)

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An x-ray structural study of the nitrato-(p-aminobenzoato)lead(II) $[Pb(H_2NC_6H_4COO)NO_3]_n$ has been carried out (diffractometer, λCu, 1520 reflections, heavy atom method, refinement by the method of least squares in the anisotropic approximation, R = 0.085). The crystals are triclinic, a = 6.933(2), b = 8.597(2), c = 7.940(2) Å, α = 102.32(2), β = 82.62(2), γ = 102.14(2)°, Z = 2, V = 450.28 Å^3, d_{calc} = 2.99 g/cm^3, space group $P\bar{1}$. The two oxygen atoms of the COO$^-$ group of p-aminobenzoic acid (PABA) are coordinated to the lead atom (Pb—O 2.53(3) and 2.51(2) Å), and also act as bridges between lead atoms (Pb—O 2.61(2) and 2.79(2) Å): the first atom and the two related to it by centers of symmetry. The coordination is brought up to eight by three oxygen atoms (Pb—O 2.65(2), 2.98(3), and 3.07(3) Å) from two NO_3^- groups and one nitrogen atom from the amino group of PABA.

We previously determined the structure of the complex of p-aminobenzoic acid (PABA) with divalent lead, of the type $[PbL_2]_n$ (where L = $H_2NC_6H_4COO^-$) (I), synthesized by the reaction of $Pb(CH_3COO)_2$ and PABA [1]. Our next aim was to obtain a complex of lead with two different ligands of the type $[PbLL']_n$ (where L = $H_2NC_6H_4COO^-$, and L' represents, in particular, NO_3^-). For this purpose we synthesized the complex of PABA with divalent lead nitrate $[Pb(H_2NC_6H_4COO)NO_3]_n$ (II). The present paper describes an x-ray structural study of complex II.

EXPERIMENTAL AND STRUCTURAL DETERMINATION

Complex II was obtained by mixing hot aqueous solutions of 0.01 M lead(II) nitrate and 0.01 M sodium p-aminobenzoate. Pale yellow crystals separated after several hours. The presence of the NO_3^- group in complex II was established in the structure determination.

The x-ray diffraction study was carried out on a "Syntex P2$_1$" automatic four-circle diffractometer (CuK$_\alpha$ radiation). The crystals of compound II are triclinic, a = 6.933(2), b = 8.597(2), c = 7.940(2), Å, α = 102.32(2), β = 82.62(2), γ = 102.14(2)α, V = 450.28 Å^3, M = 405.25, d_{calc} = 2.99 g/cm^3, Z = 2Pb$(H_2NC_6H_4COO)NO_3$, space group $P\bar{1}$.

The average volume corresponding to the chemical bond [2] is 8.34 Å^3. The intensities of 1520 reflections were measured using a crystal with dimensions 0.17 × 0.23 × 0.19 mm (θ/2θ scanning, 2θ ⩽ 120°). The reflections with $F^2 \geqslant 2\sigma$ were used in the structural calculations. All the calculations were carried out on a "Nova-1200" minicomputer using the programs of the system "Syntex XTL."

The structure was determined by the heavy atom method and refined by the method of least squares in the anisotropic approximation. The final value of R is 0.085, and the corresponding coordinates are given in Table 1 (the table of anisotropic temperature factors can be obtained from the authors).

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*For Paper V, see [1].

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TABLE 1. Coordinates of the Atoms (×10^4)

Atoms	x	y	z	Atoms	x	y	z
Pb	2842(1)	5233(1)	3587(1)	C(1)	1783(45)	2901(29)	5894(40)
O(1)	560(26)	3813(31)	5783(32)	C(2)	1124(39)	1441(32)	6656(36)
O(2)	3535(29)	3189(25)	5156(29)	C(3)	—824(46)	1060(37)	7305(41)
O(3)	7896(36)	4127(29)	—90(36)	C(4)	—1535(44)	—356(33)	7918(40)
O(4)	4892(33)	3200(32)	—738(34)	C(5)	—194(43)	—1341(32)	7943(37)
O(5)	5604(28)	3628(25)	1924(24)	C(6)	1791(41)	—927(33)	7324(40)
N(1)	—927(36)	—2816(30)	8510(34)	C(7)	2408(41)	465(38)	6726(41)
N(2)	6117(33)	3673(28)	410(39)				

TABLE 2. Bond Lengths d, Å

Bond	d	Bond	d
Pb—O(1)	2,53(3)	O(5)—N(2)	1,22(4)
Pb—O(1)*	2,61(2)	N(1)—C(5)	1,41(4)
Pb—O(2)	2,51(2)	C(1)—C(2)	1,47(4)
Pb—O(2)*	2,79(2)	C(2)—C(3)	1,38(4)
Pb—O(3)*	3,07(3)	C(2)—C(7)	1,36(4)
Pb—O(4)*	2,98(3)	C(3)—C(4)	1,38(4)
Pb—O(5)	2,65(2)	C(4)—C(5)	1,39(4)
Pb—N(1)*	2,61(3)	C(5)—C(6)	1,40(4)
O(1)—C(1)	1,29(4)	C(6)—C(7)	1,35(4)
O(2)—C(1)	1,28(4)	Average	1,38
O(3)—N(2)	1,25(4)		
O(4)—N(2)	1,27(4)		

*O(1): — x, 1 — y, 1 — x; O(2): 1 — x, 1 — y, 1 — z; O(3), O(4): 1 — x, 1 — y, — z; N(1): — x, — y, 1 — z.

TABLE 3. Valence Angles ω, deg

Angle	ω	Angle	ω	Angle	ω
O(1)PbO(2)	51,9(7)	O(1)*PbN(1)*	83,9(8)	O(3)N(2)O(5)	121,1(26)
PbO(1)C(1)	93,7(18)	O(2)PbO(2)*	79,0(7)	O(4)N(2)O(5)	121,6(26)
PbO(2)C(1)	95,1(17)	O(2)PbO(3)*	145,6(7)	Average	120
O(1)C(1)O(2)	118,5(27)	O(2)PbO(4)*	132,7(7)		
Σ	359,2	O(2)PbO(5)	66,6(7)	O(1)C(1)C(2)	121,2(26)
		O(2)PbN(1)*	87,6(8)	O(2)C(1)C(2)	119,9(26)
O(3)*PbO(4)*	41,7(7)	O(2)*PbO(3)*	115,8(7)	Average	120,6
PbO(3)*N(2)*	96,7(18)	O(2)*PbO(4)*	74,7(7)		
PbO(4)*N(2)*	100,4(18)	O(2)*PbO(5)	71,9(6)	C(1)C(2)C(3)	119,5(26)
O(3)*N(2)*O(4)*	117,3(26)	O(2)*PhN(1)*	147,4(7)	C(1)C(2)C(7)	120,8(26)
Σ	356,1	O(3)*PbO(5)	87,9(7)	Average	120,2
		O(3)*PbN(1)*	62,9(8)		
O(1)PbO(1)*	68,2(8)	O(4)*PbO(5)	68,1(7)	C(3)C(2)C(7)	119,7(28)
O(1)PbO(2)*	112,3(7)	O(4)*PbN(1)*	93,9(8)	C(2)C(3)C(4)	121,2(29)
O(1)PbO(3)*	131,3(7)	O(5)PbN(1)*	75,6(7)	C(3)C(4)C(5)	117,5(29)
O(1)PbO(4)*	173,0(7)	PbO(1)Pb†	111,8(9)	C(4)C(5)C(6)	120,9(27)
O(1)PbO(5)*	114,2(7)	Pb†O(1)C(1)	154,2(20)	C(5)C(6)C(7)	119,3(28)
O(1)PbN(1)*	80,6(8)	PbO(2)Pb*	101,0(7)	C(2)C(7)C(6)	121,2(29)
O(1)*PbO(2)	120,1(7)	Pb*O(2)C(1)	132,5(19)	Average	120
O(1)*PbO(2)*	128,5(7)	PbO(5)N(2)	166,6(19)		
O(1)*PbO(3)*	76,5(7)	PbN(1)*C(5)*	118,7(19)	N(1)C(5)C(4)	117,7(26)
O(1)*PbO(4)*	107,1(7)			N(1)C(5)C(6)	121,3(26)
O(1)*PbO(5)	158,3(7)	O(3)N(2)O(4)	117,3(26)	Average	120

*PbO(1): —x, 1 — y, 1 — z; O(2): 1 — x, 1 — y, 1 — z; N(1): —x, —y, 1 — z; O(3), O(4), N(2): 1 — x, 1 — y, —z.
†Pb: 1 — x, 1 — y, 1 — z.

DESCRIPTION OF STRUCTURE

The structure of crystal II can be represented as a three-dimensional coordination polymer. Against a background of the entire structure, however, from their pattern and compactness, it is possible to distinguish clearly defined chains consisting of Pb(II) atoms and the COO^- groups of PABA joining them to one another. This chain, which extends along [100], can be clearly seen in the projection of the structure on the plane (010) (see Fig. 1). The bond lengths and valence angles are given in Tables 2 and 3. Table 4 gives the equations of the average planes of the planar fragments of the molecule and the angles between the planes.

TABLE 4. Coefficients of the Equations of the Planes Ax + By + Cz = D of Various Planar Fragments of the Complex, and the Angles between 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(2) C(3) C4) C(5) C(6) C(7) C(1)* 0,02 —0,02 0,00 0,01 —0,00 —0,01 —0,01 0,10 Pb* O(1)* N(1)* 0,97 0,17 0,06	—0,24	—0,32	—0,92	—5,08			70,0
II	Pb O(1) O(2) C(1) C(2)* C(3)* C(4)* 0,02 —0,04 —0,04 0,06 0,44 0,67 1,12 C(5)* C(6)* C(7)* 1,28 1,01 0,58	—0,29	—0,59	—0,75	—4,78	18,3		
III	O(3) O(4) O(5) N(2) Pb* O(1)* O(2)* 0,00 0,00 0,00 —0,01 —1,91 —1,11 0,09 C(1)* C(2)* C(3)* —0,04 1,08 0,97	0,35	—0,93	—0,14	—1,55		56,9	
IV	Pb O(3) † O(4)† N(2)† O(1)* O(2)* C(1)* —0,09 0,15 0,18 —0,24 —0,30 1,13 0,65	0,41	—0,74	—0,53	—3,68	50,9	44,0	25,2

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

†1 — x, 1 — y, —z.

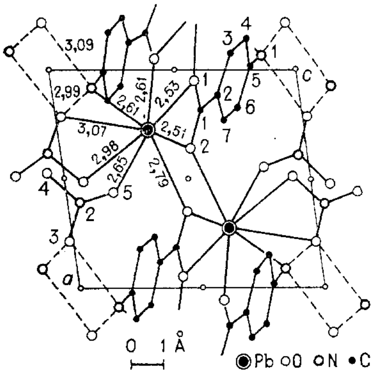

Fig. 1. Projection of the structure along [010].

The oxygen atoms of the COO^- group of the single independent PABA molecule present in the coordination sphere of the "original" Pb atom (Pb—O(1) 2.53(3), Pb—O(2) 2.51(2) Å) act simultaneously as a bridge between them and the two Pb atoms related to the first by a center of symmetry (Pb (−x, 1 − y, 1 − z) − O(1) 2.61(2), Pb (1 − x, 1 − y, 1 − z) − O(2) 2.79(2) Å). The average value of the Pb—O bond lengths, 2.61 Å, agrees with the analogous distances 2.37-2.84 Å in complex I [1], 2.59-2.94 Å in $Pb(HCOO)_2[SC(NH_2)_2]_2 \cdot H_2O$ [3], 2.37-3.01 Å in $Pb[SC(NH_2)_2](C_2H_3O_2)_2$ [4], 2.39-2.90 Å in $Pb(C_5H_4NCOO)_2$ [5], and 2.47-2.96 Å in $Pb(C_5H_4NCOO)_2 \cdot H_2O$ [6]. The sum of the internal angles of the four-membered metal-containing ring PbO(1)C(1)-O(2), 359.2°, coincides with the ideal value of 360° for a planar quadrilateral and indicates that the chelate ring is rigorously planar (plane II, Table 4). The maximum deviation of the C(1) atom from the average plane drawn through this ring is only 0.06 Å.

The nitrogen atom of the NH_2 group of PABA is present in the coordination sphere of the metal atom of the chain translationally identical to the first along the b axis. The length of the bond Pb—N(1) (−x, −y, 1 − z) 2.61(3) Å coincides within the limits of accuracy with the analogous bonds in other Pb(II) complexes [5-7]. The length of the bond N(1)—C(5) 1.41(4) Å has the usual value for a bond with an aromatic ring [8]. Thus the amine group of PABA connects the chains translationally identical along the b axis to form layers parallel to the (001) plane. These layers are joined to one another by NO_3^- groups, which are more strongly bound to the metal atom by one of their oxygen atoms (Pb—O 2.65(2) Å). This distance is smaller than the corresponding distance in $Pb(NO_3)_2$. The distance between the metal atom and the two other oxygen atoms from NO_3^- groups, 2.98(3) and 3.07(3) Å, are appreciably greater than the corresponding distance in $Pb(NO_3)_2$ [9]. With allowance for the last two oxygen atoms, the coordination number of the lead atom is 8. The coordination polyhedron is not regular. The sum of the angles at the N(2) atom of the nitrate group indicates that it has trigonal sp^2 hybridization (plane III, Table 4). These layers are additionally joined to one another by hydrogen bonds. The latter are formed between the oxygen atoms of the NO_3^- groups and the nitrogen atoms of the NH_2 groups (O...N 2.99(4) and 3.09(4) Å).

The distances between the fragments of the structure, except for those corresponding to specific interactions, have the usual van der Waals values (a table of these distances can be obtained from the authors).

Comparison of the structures of the complexes I [1] and II show an interesting similarity between them, namely the constancy of the principal motifs of the chains of Pb atoms and PABA molecules (Fig. 1 in the present work and Fig. 1 in [1]). This similarity is also reflected in the values of the crystal lattice parameters. It should be noted that among the structures determined, this group of Pb atoms and carboxylate ligands has been detected for the first time. Another feature of stereochemical interest is that the NO_3^- group, replacing one PABA molecule in complex I, acts as both a chemical and structural analog of PABA. To investigate the limit of stability of this group, that is, its dependence on the regular stereochemical features of the carboxylate ligand and additionally other ligands, it is apparently necessary to carry out the systematic preparation and study of the structure of several complexes of this kind.

LITERATURE CITED

1. I. R. Amiraslanov, N. Kh. Dzhafarov, G. N. Nadzhafov, Kh. S. Mamedov, E. M. Movsumov, and B. T. Usubaliev, Zh. Strukt. Khim., 21, 1, 131 (1980).
2. Kh. S. Mamedov and E. M. Movsumov, Azerb. Khim. Zh., 2, 83 (1976).
3. I. Goldberg and F. H. Herbstein, Acta Crystallogr., B29, 246 (1973).
4. M. Nardelli, G. Fava, and G. Branchi, Acta Crystallogr., 13, 898 (1960).
5. C. M. Biagini, M. A. Gaetani, C. Guastini, and A. Musatti, Gazz. Chim. Ital., 105, 117 (1975).
6. C. M. Biagini, M. A. Gaetani, C. Gaustini, and M. Nardelli, Gazz. Chim. Ital., 102, 1034 (1972).
7. C. S. Choi and H. P. Boutin, Acta Crystallogr., B25, 982 (1969).
8. L. E. Sutton (editor), Tables of Interatomic Distances and Configuration in Molecules and Ions. Supplement 1956-1959, Special Publication No. 18, The Chemical Society, London (1965).
9. W. C. Hamilton, Acta Crystallogr., 10, 103 (1957).

STRUCTURE OF THE DOUBLE FLUORIDE AND METANIOBATE OF POTASSIUM

$KF \cdot 4KNbO_3$.

FOUR TYPES OF COORDINATION OF THE LIGHT ATOMS IN THE STRUCTURE

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Crystals of $KF \cdot 4KNbO_3$ have been synthesized and studied by x-ray diffraction (diffractometer, 1260 reflections, anisotropic refinement, $R = 0.029$). The structure contains columns of double NbO_6 octahedra, extending in the direction of the *a* axis. The distances Nb—O in the crystallochemically independent octahedra lie in the ranges: $(NbO_6)_I$ 1.764-2.400, $(NbO_6)_{II}$ 1.770-2.411 Å.

INTRODUCTION

The extensive group of fluoride, oxide fluoride, and oxide compounds of niobium and the crystallochemically similar tantalum provides interesting material which makes it possible to follow the dependence of various details of the structure on composition or, more accurately, on the number of light atoms (O, F) corresponding to one atom of the complex-forming metal. With decrease in the ratio of the number of nonmetal atoms (O, F = X) to the number of atoms of Nb or Ta (X:M), rearrangement of the structures takes place in such a way as to ensure the more "economic" use of the available ligands. This is revealed specifically as follows.

1) With decrease in the ratio X:M from 8 to 6, the coordination number (CN) of the metal decreases from 8 to 6. For a ratio X:M = 6 or less, the coordination polyhedron becomes an octahedron (usually distorted). The polyhedra in this group of compounds are isolated from one another.

2) Further decrease in the ratio X:M leads not to a decrease in the CN but to the sharing of the ligands by two metal atoms or, in other words, to the appearance of bridging nonmetal atoms. This leads to the linking of the octahedra through their apices to form chains and rings (X:M = 5), double chains (X:M = 4.5), layers (X:M = 4-3.5), and three-dimensional frameworks (X:M = 3.25-3.00). At a ratio X:M = 3, all the apices of the octahedra are shared, and the possibilities for economy in "structural material," based on the sharing of the atoms of oxygen (or fluorine) by two metal atoms, are exhausted.

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