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

## VII.* THE CRYSTAL STRUCTURE OF $[Zn(p\text{-}H_2NC_6H_4COO)_2]_n \cdot 1.5nH_2O$

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The structure of the hydrate of bis-(p-aminobenzoato)zinc $[Zn(p\text{-}H_2NC_6H_4COO)_2]_n \cdot 1.5nH_2O$ has been studied by x-ray diffraction ($\lambda CuK_\alpha$, diffractometer, heavy-atom method, anisotropic refinement, R = 0.052). Each ligand is coordinated through the $COO^-$ and $NH_2$ ends simultaneously to two Zn atoms. The coordination of the Zn atom is tetrahedral: 2 N from different ligands, and 2O from a third and a fourth ligand. The bond lengths are Zn–N 2.058(10) and 2.053(9), Zn–O 1.979(6) and 1.943(7) Å.

An attempt by Dubsky and Trtylek [2] to prepare a complex of zinc with p-aminobenzoic acid (PABA) by the reaction of a weakly acidic buffer solution of PABA and its potassium salt with zinc sulfate was unsuccessful. Alyaviya and co-workers [3] studied complex formation by halides of the zinc group with PABA by PMR and ultraviolet spectroscopy. The first reports of complexes of PABA with zinc, and some of its physicochemical characteristics, were given in [4, 5]. The complex was assigned the chemical formula $Zn(H_2NC_6H_4COO)_2 \cdot H_2O$; it was established that it is dehydrated at 85-97°, and spectroscopic data showed that the amine and carboxylate groups of the ligand are coordinated to the zinc atom.

The aim of the present work was to establish the detailed crystal structure of the zinc complex of PABA and to investigate the interaction of the water molecules with the basic components of the structure.

* For Paper VI see [1].

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

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| Zn | 6014(2) | 6418(1) | 4613(1) | C(5) | 6654(14) | 5044(10) | 8502(5) |
| O(1) | 5182(12) | 4883(7) | 5617(4) | C(6) | 7146(16) | 6126(10) | 8194(6) |
| O(2) | 6348(10) | 6687(6) | 5762(3) | C(7) | 6833(15) | 6349(10) | 7389(6) |
| O(3) | 6773(12) | 7764(6) | 3971(4) | C(8) | 6264(14) | 8843(10) | 3953(6) |
| O(4) | 5801(12) | 9446(7) | 4540(4) | C(9) | 6294(14) | 9416(9) | 3140(5) |
| N(1) | 7035(13) | 4795(8) | 9358(4) | C(10) | 6987(14) | 8820(8) | 2486(6) |
| N(2) | 6413(11) | 11089(7) | 868(4) | C(11) | 7024(14) | 9309(9) | 1748(6) |
| C(1) | 5826(14) | 5662(10) | 6041(5) | C(12) | 6349(13) | 10554(9) | 1646(5) |
| C(2) | 6096(15) | 5455(10) | 6930(5) | C(13) | 5608(14) | 11100(8) | 2296(6) |
| C(3) | 5589(14) | 4356(10) | 7249(6) | C(14) | 5588(14) | 10578(9) | 3024(5) |
| C(4) | 5866(14) | 4154(9) | 8047(5) | | | | |

TABLE 2. Valence Angles $\omega$, deg

| Angle | ω | Angle | ω | Angle | ω |
|---|---|---|---|---|---|
| O(2)ZnO(3) | 113,0(3) | C(4)C(5)C(6) | 123(1) | C(8)C(9)C(10) | 120(2) |
| O(2)ZnN(1′) | 102,3(3) | C(5)C(6)C(7) | 119(1) | C(8)C(9)C(14) | 124(2) |
| O(2)ZnN(2′) | 122,0(3) | C(6)C(7)C(2) | 119(1) | | |
| O(3)ZnN(1′) | 100,3(3) | Average | 120 | C(10)C(9)C(14) | 118(1) |
| O(3)ZnN(2′) | 100,8(3) | | | C(9)C(10)C(11) | 123(1) |
| N(1′)ZnN(2′) | 116,8(3) | O(1)C(1)O(2) | 122(1) | C(10)C(11)C(12) | 118(1) |
| ZnO(2)C(1) | 100,4(6) | O(1)C(1)C(2) | 121(2) | C(11)C(12)C(13) | 119(1) |
| ZnO(3)C(8) | 131,3(7) | O(2)C(1)C(2) | 115(2) | C(12)C(13)C(14) | 121(1) |
| C(5)N(1)Zn(III′) | 117,6(6) | C(1)C(2)C(7) | 120(2) | C(13)C(14)C(9) | 121(1) |
| C(12)N(2)Zn(II) | 113,8(6) | N(1)C(5)C(4) | 119(1) | Average | 120 |
| | | N(1)C(5)C(6) | 119(1) | | |
| C(3)C(2)C(7) | 122(1) | O(3)C(8)O(4) | 126(1) | N(2)C(12)C(11) | 120(2) |
| C(2)C(3)C(4) | 119(1) | O(3)C(8)C(9) | 116(2) | N(2)C(12)C(13) | 122(2) |
| C(3)C(4)C(5) | 119(1) | O(4)C(8)C(9) | 115(2) | | |

* Complex II in the position 1−x, y−1/2, 1/2−z, complex III′ in the position 3/2−x, 2−y, 1/2+z.

## EXPERMENTAL

The hydrate of bis(p-aminobenzoato)zinc $[Zn(p\text{-}H_2NC_6H_4COO)_2]n \cdot 1.5nH_2O$ was obtained by adding a hot dilute aqueous solution of the sodium salt of PABA to a dilute solution of zinc sulfate. After filtering, the pale-yellow solution was left to stand for several days, after which pale-yellow crystals formed. These were separated and dried in a desiccator over anhydrous $CaCl_2$ at room temperature.

To obtain the crystallographic data, we selected a crystal with dimensions $0.2 \times 0.22 \times 0.81$ mm, elongated along the axis of rotation $a$. The parameters of the orthorhombic cell were determined on an automatic four-circle "Syntex $P2_1$" diffractometer: $a = 7.623(1)$, $b = 11.189(3)$, $c = 16.873(5)$ Å, $V = 1439$ Å$^3$, $M = 364.53$, $d_{calc} = 1.68$ g/cm$^3$, $Z = 4[Zn(p\text{-}H_2NC_6H_4COO)_2 \cdot 1.5H_2O]$, space group $P2_12_12_1$. The average volume corresponding to one chemical bond is 8.99 Å$^3$.

The determination and refinement of the structure were carried out using 1070 independent nonzero reflections with $I \geq 2\sigma$, recorded on the same diffractometer ($\lambda CuK_\alpha$, graphite monochromator). All the calculations were carried out on a "Nova 1200" minicomputer using the program "Syntex XTL."

The structure was determined by the heavy-atom method. The refinement was carried out by the method of least squares in the anisotropic approximation. The final value of $R = 0.052$; the corresponding coordinates are given in Table 1.*

## DESCRIPTION OF THE STRUCTURE

Analysis of the results obtained shows that the hydrate of bis-(p-aminobenzoato)zinc is a three-dimensional coordination polyhedron. The arrangement of the ligands in the cell and their relation to the Zn atoms are shown in Fig. 1. The bond lengths are given in Fig. 2. Table 2 gives the valence angles, and Table 3 gives the equations of the average planes of the planar fragments of the molecule.

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

TABLE 3. Coefficients of the Equations of the Planes $Ax + By + Cz = D$ for the Phenyl Rings and Various Planar Fragments of the Molecule, the Deviations of the Atoms from these Planes, and the Angles between Individual Planes (absolute coordinates)

| Plane | Atoms and their deviations from the plane, Å | | | | | | | A | B | C | D | Angles with the planes, deg | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | II | III | IV |
| I | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | Zn* | 0,91 | —0,37 | —0,21 | —0,53 | 7,9 | 135,5 | 128,7 |
| | 0,01 | 0 | —0,01 | 0 | 0,01 | —0,01 | 0,38 | | | | | | | |
| | O(1)* | O(2)* | C(1)* | N(1)* | O(3)* | C(12)* | N(2)* | | | | | | | |
| | 0,08 | 0,09 | 0,06 | 0,07 | 0,58 | —0,04 | 0,06 | | | | | | | |
| II | Zn | O(1) | O(2) | C(1) | C(2)* | C(3)* | O(3)* | 0,92 | —0,40 | —0,08 | 0,76 | | 137,1 | |
| | 0,01 | —0,02 | —0,02 | 0,03 | 0,2 | 0,29 | 0,03 | | | | | | | |
| | O(4)* | C(8)* | | | | | | | | | | | | |
| | —1,47 | —0,8 | | | | | | | | | | | | |
| III | O(3) | O(4) | C(8) | Zn* | C(9)* | C(10)* | C(11)* | 0,94 | —0,31 | —0,13 | —8,30 | | | 7,1 |
| | 0 | 0 | 0 | 0,87 | —0,04 | —0,2 | —0,23 | | | | | | | |
| | C(13)* | C(14)* | | | | | | | | | | | | |
| | 0,06 | 0,09 | | | | | | | | | | | | |
| IV | C(9) | C(10) | C(11) | C(12) | C(13) | C(14) | Zn* | —0,90 | —0,39 | —0,21 | —9,49 | 130,7 | | |
| | —0,01 | 0 | 0,02 | —0,03 | 0,02 | 0 | 0,97 | | | | | | | |
| | O(1)* | O(2)* | O(3)* | O(4)* | C(8)* | N(2)* | | | | | | | | |
| | 1,86 | 0,23 | 0,09 | —0,18 | —0,03 | —0,03 | | | | | | | | |

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

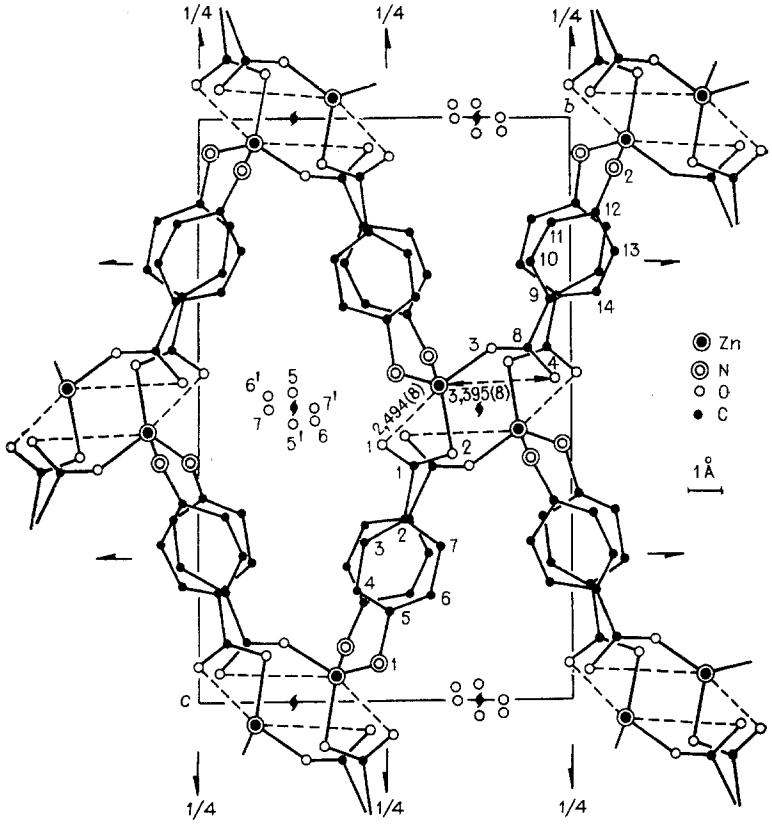


Fig. 1. Projection of the structure along [100].

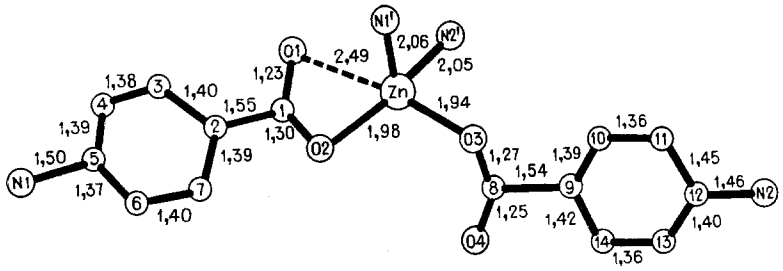


Fig. 2. Geometry of the molecule (the maximum standard deviations for the lengths of the bonds Zn–O, N and the bonds between the light atoms are 0.010 and 0.015 Å, respectively).

The three-dimensional framework of the coordination polymer is penetrated by channels parallel to the *a* axis (see Fig. 1). The water molecules are situated in these channels, and this explains the zeolite-like reversible dehydration: At 85-97°, dehydration takes place without breakdown of the crystal structure. This characteristic feature of the compound was established by high-temperature diffractometry on a GPVT-1500 assembly (conditions of the recording: DRON-1.5 apparatus, $CuK_{\alpha}$ radiation, Ni filter, I = 20 mA, V = 30 kV) (Fig. 3). As expected, the water molecules are arranged in disordered fashion in the channels, being distributed randomly in six positions [O(5): x = 0.9320(39), y = 0.2469(28), z = 0.4889(19), O(6): x = 0.2579(39), y = 0.3098(25), z = 0.5206(18), O(7): x = 0.5816(43), y = 0.1980(26), z = 0.4956(19), O(5'), O(6'), O(7') 1/2 + x, 1/2 – y, 1 – z, respectively]. It should be noted that these positions are convenient for the formation of hydrogen bonds with the ligand donors (see below).

In agreement with [4, 5], the anion of PABA is joined to the metal atom through both donor ends. The zinc atom is at the center of a distorted tetrahedron formed by two nitrogen atoms from different ligands [Zn–N(1') 2.058(10), Zn–N(2') 2.053(9) Å] and two oxygen atoms from two different ligands [Zn–O(2) 1.979(6), Zn–O(3) 1.943(7) Å]. The valence angles at the Zn atom lie in the range 100.3(3)-122.0(3)°. The average values of the bond lengths Zn–N 2.056 and Zn–O 1.961 Å are close to those found in other zinc complexes [7-23]. The

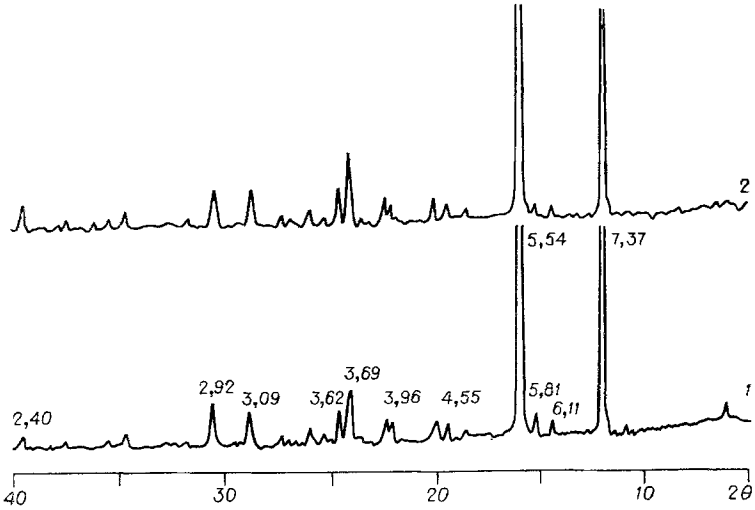


Fig. 3. Diffraction patterns of the complex (1–20°, 2–100°).

distance Zn...O(1) 2.494(8) Å is much greater than the sum of the corresponding ionic radii (2.14 Å) [24], that is the $COO^-$ group of PABA does not form a chelate with the metal atom, as observed in the cadmium complex of PABA [25]. The oxygen atoms O(1) and O(4) of the carboxylate groups of PABA not present in the coordination sphere of Zn are situated at distances from the water molecules equal to the length of an H-bond [O(1)...O(5') 2.84(3), O(1)...O(6) 2.90(3) and O(4) (x, y–1, z)...O(7) 2.92(3) Å].

The average values of the C–C bond lengths in the phenyl rings are 1.39 and 1.40 Å; these rings are planar, with a maximum deviation of 0.03 Å (see Table 3). The angles between the planes of the carboxylate groups and the phenyl rings in the PABA anions are 7.9 and 7.1°.

The short intermolecular distances are close to or greater than the sums of the corresponding van der Waals radii.

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