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

III.* THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(p-AMINOBENZOATO)TRIAQUOCADMIUM(II)

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An x-ray structural study of bis(p-aminobenzoato)triaquocadmium(II) $Cd(H_2NC_6H_4COO)_2 \cdot 3H_2O$ has been carried out (λCuK_α, automatic diffractometer, heavy-atom method, anisotropic refinement). The crystals are triclinic, $a = 17.798(4)$, $b = 6.187(1)$, $c = 8.261(2)$ Å, $\alpha = 111.98(2)$, $\beta = 105.00(2)$, $\gamma = 89.98(2)°$, $d_{calc} = 1.80$ g/cm³, $V = 810.05$ Å³, space group $P\bar{1}$, $Z = 2$, $R = 0.063$. The coordination number of the cadmium atom is 7; two chelate rings are formed with two carboxylate ligands (Cd–O(1) 2.35(1), –O(2) 2.35(1), – O(3) 2.43(1), – O(4) 2.43(1) Å), and the nitrogen atoms of the amino-groups of two neighboring complexes are coordinated in the axial positions, forming a polymeric chain along the a axis (Cd–N(1) 2.44(2), –N(2) 2.43(2) Å). The coordination is brought up to 7 by one water molecule (Cd–O(7) 2.38(1) Å), which together with the other water molecules not present in the coordination sphere connect the polymeric chains together by hydrogen bonds.

The reaction of weakly acidic buffer solutions containing aminobenzoic acids and the corresponding potassium salts together with cadmium and zinc sulfates [2] has been used to prepare the complexes of cadmium with all the isomers of aminobenzoic acid. The complex compounds formed by cadmium halides with p-aminobenzoic acid have been synthesized, and their properties have been studied by NMR and infrared spectroscopy [3-6].

The crystalline hydrate of cadmium(II) p-aminobenzoate has been prepared [7-9]. The presence of water of crystallization was proved by thermogravimetric analysis. The complex was assigned the formula $Cd(H_2NC_6H_4COO)_2 \cdot 3H_2O$. The structure was studied by infrared spectroscopy, thermal analysis, and magnetic susceptibility measurements. The spectroscopic data indicated that the amino groups and carboxyl groups of the ligand are coordinated to the cadmium atom. In the works cited, however, the coordination number and environment of the cadmium atom, and the part played by water molecules in the coordination to the central atom, were not determined. The present x-ray diffraction study was carried out to determine these characteristics.

EXPERIMENTAL

Crystals of bis(p-aminobenzoato)triaquocadmium (A) were obtained by the reaction of aqueous solutions of sodium p-aminobenzoate and $CdCl_2$.

The parameters of the triclinic cell were determined on an automatic "Syntex $P2_1$" diffractometer: $a = 17.798(4)$, $b = 6.187(1)$, $c = 8.261(2)$ Å, $\alpha = 111.98(2)$, $\beta = 105.00(2)$, $\gamma = 89.98(2)°$, $d_{calc} = 1.80$ g/cm³, $V = 810.05$ Å³, $M = 438.58$, $Z = 2$, space group $P\bar{1}$.

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*For Paper II see [1].

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

Atoms	*x*	*y*	*z*	Atoms	*x*	*y*	*z*
Cd	2500(1)	1738(2)	—1(2)	C(3)	—456(11)	2101(29)	3087(24)
O(1)	3409(7)	1389(19)	—1675(16)	C(4)	—743(10)	—168(32)	2748(24)
O(2)	1583(7)	3053(19)	1660(16)	C(5)	—255(12)	—2105(32)	2173(27)
O(3)	1802(8)	—616(21)	1045(20)	C(6)	430(10)	—1672(30)	1870(26)
O(4)	3211(7)	—1643(21)	—1023(20)	C(7)	1403(10)	1014(31)	1634(23)
O(5)	2829(10)	1930(35)	5193(25)	C(8)	3596(10)	—647(30)	—1636(23)
O(6)	2157(10)	6738(28)	4814(24)	C(9)	4276(10)	—1517(29)	—2163(23)
O(7)	2482(13)	5568(27)	—33(34)	C(10)	4557(11)	—3541(28)	—1869(26)
N(1)	6485(9)	—3534(26)	—2875(21)	C(11)	5283(11)	—4243(30)	—2153(26)
N(2)	—1489(5)	—676(27)	2873(21)	C(12)	5730(10)	—2925(30)	—2720(23)
C(1)	714(10)	642(29)	2177(24)	C(13)	5445(11)	—978(30)	—3194(25)
C(2)	284(10)	2477(28)	2802(25)	C(14)	4717(11)	—315(30)	—2800(24)

The determination and refinement of the structure were carried out using 1602 independent reflections with $I > 2\sigma$, measured on the same diffractometer (λCuK_α, graphite monochromator). All the calculations were carried out on a "Nova-1200" minicomputer using the "XTL Syntex" programs.

The coordinates of the cadmium atom were determined from the three-dimensional Patterson function; R = 0.29 after two cycles of the isotropic refinement. The difference three-dimensional ρ-synthesis revealed all the oxygen atoms of the chelating carboxyl groups (R = 0.18). The next two ρ-syntheses revealed all the atoms in the molecule of the complex other than hydrogen (R = 0.15). The difference synthesis after two cycles of the isotropic refinement of the atoms already found revealed the oxygen atoms of the three water molecules. The isotropic refinement of all atoms other than hydrogen decreased R to 0.092. Two cycles of the anisotropic refinement gave R = 0.063. Unfortunately, the hydrogen atoms could not be located by the difference synthesis. The coordinates of the atoms other than hydrogen are given in Table 1.*

DESCRIPTION OF THE STRUCTURE

Complex A has the structure of a coordination polymer, made up of monomeric units ($[Cd(H_2N - C_6H_4 - CO_2)_2 \cdot H_2O]2H_2O$). The arrangement of the molecules in the crystal is shown in Fig. 1, and 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 fragment of the molecule.

The coordination number of the cadmium atom is 7; two chelate rings are formed with two carboxylate ligands (Cd — O(1) 2.35 (1), — O(2) 2.35(1), — O(3) 2.43(1), — O(4) 2.43(1) Å), and the nitrogen atoms of the amino groups of two neighboring complexes are coordinated in the axial positions, forming a polymeric chain along the a axis (Cd — N(1) 2.44(2), — N(2) 2.43(2) Å). The coordination number is brought up to 7 by one water molecule (Cd — O(7) 2.38(1) Å). This molecule, together with the other molecules not present in the coordination sphere of the metal atom (corresponding distances Cd...O(5) and Cd...O(6) greater than 4 Å) connect the polymeric chains together by hydrogen bonds (Table 5).

We were unable, however, to determine the positions of the H atoms: the difference electron density synthesis did not give the positions of these atoms accurately, apparently because of the poor quality of the crystal and the neglect of experimental absorption factors. The positions of the hydrogen atoms on the nitrogen atom of the amino group cannot be determined from geometric considerations, since the contributions of sp^2 and sp^3 hybridization are not known. The observed O...O distances, however, correspond to the typical values for the H-bonds in the structure of cadmium(II) formate [10] and acetate [11], and give grounds for assuming that the structure being studied contains hydrogen bonds. The O...N distances are also comparable with those in bis(p-aminobenzoato)tetra-aquomanganese(II) [12].

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

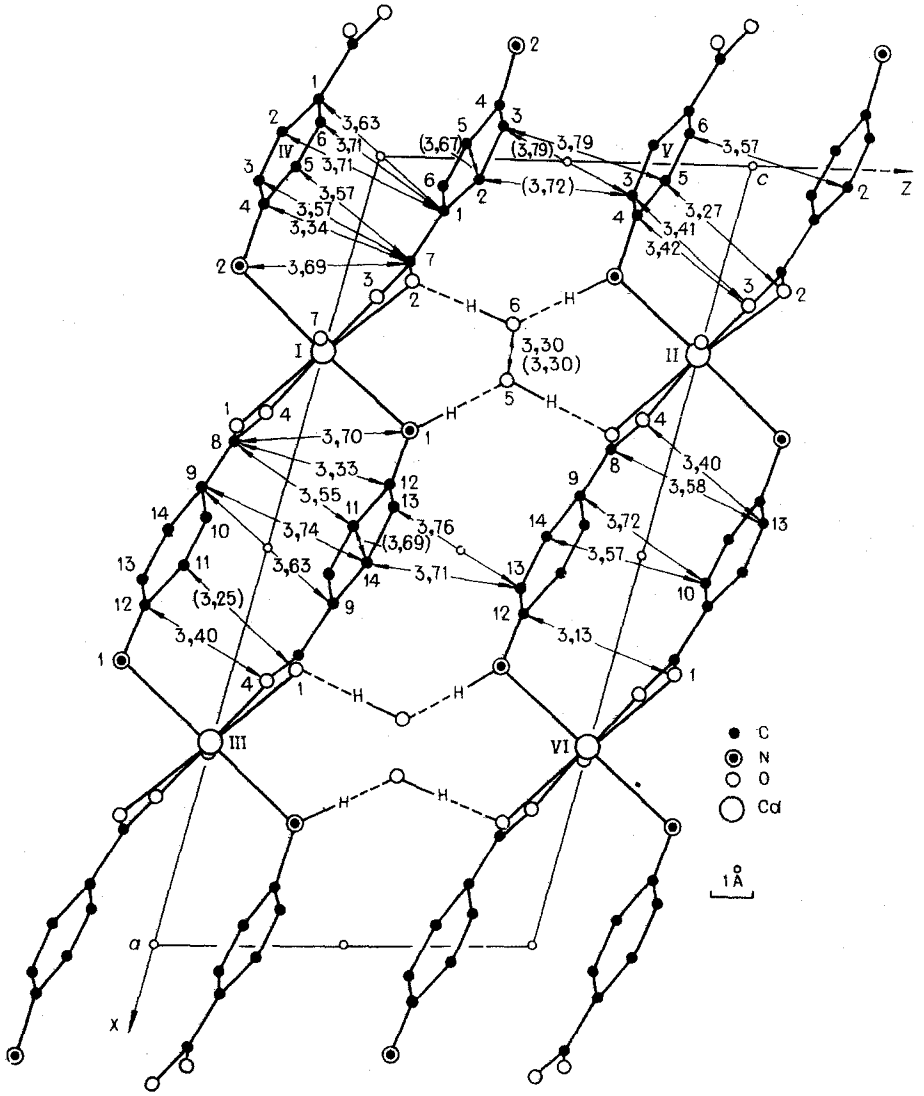

Fig. 1. Crystal structure (view along [0.1]). The figures in parentheses give the distances to the atoms, derived with the participation of the translation *b* . Original complex I at x, y, z; II at x, y, 1 + z; III at 1 − x, −y, −z; IV at −x, −y, −z; V at −x, −y, 1 − z; VI at 1 − x, −y, 1 − z.

Thus these analogies indicate the existence of strong hydrogen bonds of the type N—H... $\mathrm{OH_2}$ and H—O—H... $\mathrm{O}{<}^{\mathrm{Cd}}_{\mathrm{C}}$, which apparently play a significant role in the structure of these crystals.

The differences in the lengths of the bonds C(8)—O(4) 1.23(2) and C(8)—O(1) 1.31(2) Å, and C(7)—O(3) 1.25(2) and C(7)—O(2) 1.29(2)Å agree with published data [11] and are responsible for the difference in the lengths of the bonds Cd—O(4) 2.43(1) and Cd—O(1) 2.35(1) Å and Cd—O(3) 2.43(1) and Cd—O(2) 2.35(1) Å.

The internal angles in the chelate rings CdOC (95, 94, 92, and 93°), OCdO (118 and 118°), and OCdO (54.2 and 54.6°) are comparable with those found in the structure of $\mathrm{Cd(AcO)_2 \cdot 2H_2O}$ [11]. The sums of the internal angles in the two chelate rings are 360.2 and 358.2° respectively.

The average value of the C—C bond lengths in the phenyl rings is 1.41 Å; these rings are planar, with a maximum deviation of 0.03 Å (see Table 4).

All the intermolecular distances are equal to or greater than the sums of the correspond-

TABLE 2. Bond Lengths d (Å)

Bond	d	Bond	d
Cd—O(1)	2,35(1)	C(1)—C(2)	1,38(3)
Cd—O(2)	2,35(1)	C(2)—C(3)	1,43(3)
Cd—O(3)	2,43(1)	C(3)—C(4)	1,39(3)
Cd—O(4)	2,43(1)	C(4)—C(5)	1,48(3)
Cd—O(7)	2,38(1)	C(5)—C(6)	1,35(3)
Cd—N(1)	2,44(2)	C(6)—C(1)	1,43(3)
Cd—N(2)	2,43(2)	Average	1,41
O(1)—C(8)	1,31(2)		
O(2)—C(7)	1,29(2)	C(9)—C(10)	1,43(3)
O(3)—C(7)	1,25(2)	C(10)—C(11)	1,41(3)
O(4)—C(8)	1,23(2)	C(11)—C(12)	1,41(3)
N(1)—C(12)	1,42(3)	C(12)—C(13)	1,42(3)
N(2)—C(4)	1,40(3)	C(13)—C(14)	1,41(3)
C(1)—C(7)	1,46(3)	C(14)—C(9)	1,40(3)
C(8)—C(9)	1,43(3)	Average	1,41

TABLE 3. Valence Angles ω (deg)

Angle	ω	Angle	ω	Angle	ω
O(1)CdO(2)	165,3(4)	N(1)CdN(2)	169,4(5)	N(2)C(4)C(3)	121(2)
O(1)CdO(3)	140,1(5)	CdO(1)C(8)	95(1)	N(2)C(4)C(5)	121(2)
O(1)CdO(4)	54,2(5)	CdO(2)C(7)	94(1)		
O(1)CdO(7)	83,0(7)	CdO(3)C(7)	92(1)	C(9)C(10)C(11)	120(2)
O(1)CdN(1)	91,7(5)	CdO(4)C(8)	93(1)	C(10)C(11)C(12)	121(2)
O(1)CdN(2)	86,7(5)	C(12)N(1)Cd(III)	112(1)	C(11)C(12)C(13)	119(2)
O(2)CdO(3)	54,6(5)	CdN(2)C(4)(IV)	113(1)	C(12)C(13)C(14)	119(2)
O(2)CdO(4)	140,5(5)	C(6)C(1)C(7)	121(2)	C(13)C(14)C(9)	122(2)
O(2)CdO(7)	82,3(7)	C(2)C(1)C(7)	120(2)	C(10)C(9)C(14)	119(2)
O(2)CdN(1)	86,9(5)			Average	120
O(2)CdN(2)	91,9(5)	C(2)C(1)C(6)	118(2)		
O(3)CdO(4)	86,3(5)	C(1)C(2)C(3)	123(2)	O(2)C(7)O(3)	118(2)
O(3)CdO(7)	136,7(7)	C(2)C(3)C(4)	118(2)	C(1)C(7)O(2)	119(2)
O(3)CdN(1)	95,0(5)	C(3)C(4)C(5)	119(2)	C(1)C(7)O(3)	122(2)
O(3)CdN(2)	93,0(5)	C(4)C(5)C(6)	121(2)	O(1)C(8)O(4)	118(2)
O(4)CdO(7)	137,0(7)	C(5)C(6)C(1)	122(2)	O(1)C(8)C(9)	119(2)
O(4)CdN(1)	92,2(5)			O(4)C(8)C(9)	122(2)
O(4)CdN(2)	95,4(5)	Average	120	C(8)C(9)C(10)	120(2)
O(7)CdN(1)	85,3(7)	N(1)C(12)C(11)	121(2)	C(8)C(9)C(14)	121(2)
O(7)CdN(2)	84,1(7)	N(1)C(12)C(13)	120(2)		

TABLE 4. The Coefficients of the Equations of the Planes Ax + By + Cz = D for Various Planar Fragments of the Molecule, the Deviation of the Atoms from These Planes, and the Angles between the Individual Planes (absolute coordinates)

Plane	*A*	*B*	*C*	*D*	Atoms and their deviations from the plane in Å								Angle with the planes, deg		
													I	II	III
I	—0,30	—0,25	—0,92	—1,65	C(2) —0,01	C(3) —0,01	C(4) 0,03	C(5) —0,03	C(6) 0,01	C(1) 0,01	O(2)* 0,38	O(3)* 0,27		22,4	
					O(7)* 1,55	N(2)* 0,12	C(7)* 0,19	Cd * 1,04							
II	—0,29	—0,60	—0,75	—3,42	C(9) 0,02	C(10) 0	C(11) —0,01	C(12) 0,02	C(13) 0	C(14) —0,01	O(1)* 0,40	O(4)* 0,25			25,2
					O(5)* —0,69	O(6)* —0,94	N(1)* 0,11	C(8)* 0,18	Cd * 2,30						
III	—0,61	0,31	—0,73	—2,25	Cd 0	O(2) 0	O(3) 0	O(7)* 0,17	C(1)* 0,43	C(7)* 0,10	O(1)* —4,80	O(4)* —4,54	21,2		
IV	—0,02	—0,60	—0,80	0,13	Cd 0	O(1) 0	O(4) 0	O(3)* —0,40	O(7)* —0,49	C(8)* —0,28	O(2)* —1,27	O(3)* —0,40	27,0	15,7	38,9

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

TABLE 5. Hydrogen Bonds A–H...B (d is the distance A...B)

Bond	d, Å	Angle	ω,°
O(5) ... N(1)*	2,96(2)	N(1)*O(5)O(1)*	134,2(3)
O(5) ... O(1)*	2,68(2)		
O(6) ... O(2)	2,68(2)	O(2)O(6)N(2)*	135,8(3)
O(6) ... N(2)*	2,95(3)		
O(7) ... O(3)*	2,61(1)	O(3)*O(7)O(4)*	78,3(3)
O(7) ... O(4)*	2,63(1)		

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

ing van der Waals radii of the atoms (see Fig. 1). The volume corresponding to one chemical bond, calculated by the published method [14], is 9.0 $Å^3$.

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