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Synthesis and Crystal Structure of 18-Crown-6 *E*-2-Phenylethenylphosphonic Acid Diaqua(18-crown-6)sodium *E*-2-Phenylethenylphosphonate

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Abstract—New complex compound, diaqua(18-crown-6)sodium *E*-2-phenylethenylphosphonate 18-crown-6 *E*-2-phenylethenylphosphonic acid, $[Na(18\text{-crown-6})(H_2O)_2]^+ \cdot HO_3^-PCH{=}CHPh \cdot 18\text{-crown-6} \cdot H_2O_3PCH{=}CHPh$, was obtained and its crystal and molecular structures were studied by the X-ray structural analysis. In this structure the complex cation $[Na(18\text{-crown-6})(H_2O)_2]^+$ is of *guest–host* type. The coordination polyhedron of its Na^+ cation is a slightly screwed hexagonal bipyramid with the base consisting of all 6 O atoms of 18-crown-6 ligand and with two opposite apexes at two O atoms of two ligand water molecules. In the studied crystal structure the alternating complex cations and 18-crown-6 molecules as well as the molecules of acid and its anion $HO_3^-PCH{=}CHPh$ form by means of hydrogen bonds the infinite chains of two different types.

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In this article are described peparation and results of X-ray structural analysis of new complex compound, 18-crown-6 *E*-2-phenylethenylphosphonic acid diaqua(18-crown-6)sodium *E*-2-phenylethenylphosphonate $[Na(18\text{-crown-6})(H_2O)_2]^+ \cdot HO_3^-PCH{=}CHPh \cdot 18\text{-crown-6} \cdot H_2O_3PCH{=}CHPh$ (**I**). Earlier by the method of X-ray structural analysis crystal and molecular structures of unsubstituted *E*-2-phenyl-ethenylphosphonic acid $H_2O_3PCH{=}CHPh$ [1] and crystal structure of its monosodium salt, sodium hydrogen *E*-2-phenyl-ethenylphosphonate, $NaHO_3PCH{=}CHPh$ (**II**) were studied [2].

Asymmetric part of the unit cell of crystals **I** contains one complex cation $[Na(18\text{-crown-6})(H_2O)_2]^+$ of *guest–host* type [3], one $HO_3^-PCH{=}CHPh$ anion, one 18-crown-6 molecule and one molecule of $H_2O_3 \cdot PCH{=}CHPh$. The molecular–ionic structure of the complex compound **I** in crystal is shown in the figure; the basic bond lengths and bond angles are listed in Tables 1 and 2.

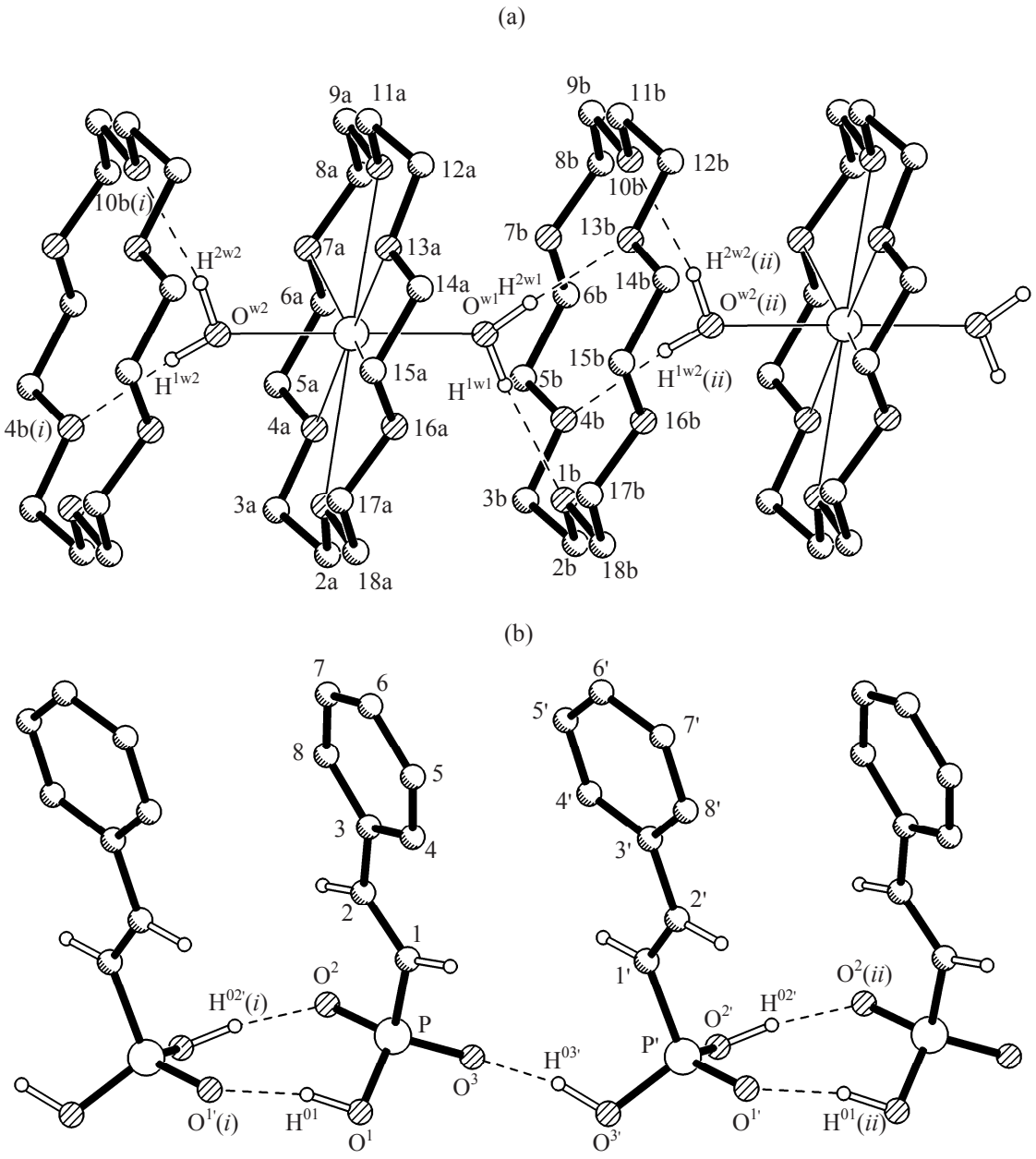
In the structure **I** the Na^+ cation of complex $[Na(18\text{-crown-6})(H_2O)_2]^+$ cation is located in the cavity of 18-crown-6 ligand and is coordinated by all 6 O atoms of the ligand and two O atoms of two ligand water molecules. The coordination polyhedron of this Na^+ cation (coordination number 8) is a slightly screwed hexagonal bipyramid with the base consisting of all 6 O atoms of 18-crown-6 ligand and with two opposite apexes at O^{w1} and O^{w2} atoms. This Na^+ cation is located exactly in the mean square plane of 6 O atoms of its 18-crown-6 ligand (a).

In the structure **I**, the average bond length over all 8 coordination Na–O bonds equals 2.674±0.174 Å and

Table 1. Main bond lengths (*d*, Å) in structure **I**[a]

Bond	*d*	Bond	*d*
$Na–O^{1a}$	2.730(4)	$Na–O^{13a}$	2.702(4)
$Na–O^{4a}$	2.774(5)	$Na–O^{16a}$	2.998(5)
$Na–O^{7a}$	2.859(5)	$Na–O^{w1}$	2.348(4)
$Na–O^{10a}$	2.651(4)	$Na–O^{w2}$	2.326(4)
$P–O^{1}$	1.562(4)	$P'–O^{1'}$	1.509(3)
$P–O^{2}$	1.530(3)	$P'–O^{2'}$	1.552(4)
$P–O^{3}$	1.496(4)	$P'–O^{3'}$	1.538(4)
$P–C^{1}$	1.779(4)	$P'–C^{1'}$	1.771(4)
$C^{1}=C^{2}$	1.317(5)	$C^{1'}=C^{2'}$	1.320(5)

[a] In Tables 1, 2 and 3 the atoms in the *E*-2-phenylethenyl-phosphonic acid molecule are primed, the atoms in the anion are unprimed.



Molecular-ionic structure of complex compound **I** in crystal. (a) Infinite (along *x* axis) chain of alternating complex cations $[Na(18\text{-crown-6})(H_2O)_2]^+$ and 18-crown-6 molecules. (b) Infinite (along *x* axis) chain of alternation $HO_3PCH{=}CHPh$ anions and $H_2O_3PCH{=}CHPh$ molecules. The H atoms at the 18-crown-6 ligands and molecules and phenyl rings are omitted for clarity. Hydrogen bonds are indicated by dashed lines.

is close to the sum of effective ionic radius of Na^+ cation (1.18 Å for coord. no. 8) [4] and van der Waals radius of oxygen atom, 1.40–1.52 Å [5, 6]. Both its axial bonds $Na–O^{w1}$ and $Na–O^{w2}$ are much shorter than this average value, and two (of six) equatorial $Na–O^{7a}$ and $Na–O^{16a}$ bonds are much longer than the mentioned common bond length averaged over all eight Na–O bonds.

In the structure **I** the 18-crown-6 ligand (a) in this conformation (see below) has a cavity too spacious for Na^+ cation. Therefore two noted above $Na–O^{7a}$ and

Table 2. Principal bond angles (ω, deg) in structure **I**

Angle	ω	Angle	ω
$O^{1a}NaO^{10a}$	179.3(2)	$O^{w1}NaO^{7a}$	79.3(1)
$O^{4a}NaO^{13a}$	177.2(2)	$O^{w1}NaO^{10a}$	80.1(1)
$O^{7a}NaO^{16a}$	178.5(1)	$O^{w1}NaO^{13a}$	102.1(2)
$O^{1a}NaO^{16a}$	59.6(1)	$O^{w1}NaO^{16a}$	101.3(1)
$O^{1a}NaO^{4a}$	59.9(1)	$O^{w2}NaO^{1a}$	79.9(1)
$O^{4a}NaO^{7a}$	60.2(1)	$O^{w2}NaO^{4a}$	100.4(2)
$O^{7a}NaO^{10a}$	61.6(1)	$O^{w2}NaO^{7a}$	100.0(2)
$O^{10a}NaO^{13a}$	62.3(1)	$O^{w2}NaO^{10a}$	100.5(1)
$O^{13a}NaO^{16a}$	58.7(1)	$O^{w2}NaO^{13a}$	79.3(2)
$O^{w1}NaO^{1a}$	99.5(1)	$O^{w2}NaO^{16a}$	79.5(2)
$O^{w1}NaO^{4a}$	78.3(2)	$O^{w1}NaO^{w\,2}$	178.7(2)
$O^{1}PO^{2}$	109.8(2)	$O^{1'}P'O^{2'}$	111.8(2)
$O^{1}PO^{3}$	109.3(2)	$O^{1'}P'O^{3'}$	111.8(2)
$O^{2}PO^{3}$	114.3(2)	$O^{2'}P'O^{3'}$	107.9(2)
$O^{1}PC^{1}$	105.6(2)	$O^{1'}P'C^{1'}$	110.4(2)
$O^{2}PC^{1}$	106.8(2)	$O^{2'}P'C^{1'}$	108.1(2)
$O^{3}PC^{1}$	110.6(2)	$O^{3'}P'C^{1'}$	106.7(2)

Na–O^{16a} bonds are very weak (elongated) coordination bonds and even can be considered as not existing (the last one in particular).

In the structure **I** the geometric structures of 18-crown-6 ligand (a) and 18-crown-6 molecule (b) are very similar. They both are in conformation of screwed crown with approximately D_{3d} symmetry. In such conformation the six O atoms of (a) and (b) are alternately deviated to the opposite sides from their mean square plane, average by (a) ±0.174 and (b) ±0.242 Å . In these 18-crown-6 ligand and molecule all torsion angles O–C–C–O are synclinal (*gauche* type) and alternately are close to (a) ±66° and (b) ±70°; all other C–O–C–C torsion angles are anti-periplanar (*trans* type) in the range 180 ± 13°. It is seen that in the structure **I** the 18-crown-6 ligand (a) is more flattened than the 18-crown-6 molecule (b).

In the structure **I** the respective covalent bond lengths in the 18-crown-6 ligand and molecule are close by value. The O–C average bond length [1.416 (4) Å] is a bit shorter than the average statistical value 1.426(11) Å for the fragments C#–O–CH_2–C#, and average C–C bond length [1.486(5) Å] is considerably less than the statistically averaged (for the C#–CH_2–CH_2–C# fragment) value 1.524(14) Å [7]. Such effective shortening of intracyclic C–C bonds is well known for 18-crown-6 ligands and molecule [3, 8]. It is also noteworthy that in these 18-crown-6 ligand and molecule (a and b) all bond angles C–O–C (average 112.2°) are larger and O–C–C bond angles are slightly less or slightly larger than the ideal tetrahedral angle 109.5°

Table 3. Geometric parameters of intermolecular (interionic) hydrogen bonds in the crystal structure **I**[a]

H bond	Distance, Å			Angle, deg
O–H···O	O–H	H···O	O···O	O–H···O
O^{1}–H^{01}···$O^{1'}$(*i*)	0.95(2)	1.68(3)	2.609(5)	165(4)
$O^{2'}$–$H^{02'}$···O^{2}(*ii*)	0.95(2)	1.56(3)	2.502(4)	169(4)
$O^{3'}$–$H^{03'}$···O^{3}	0.95(2)	1.61(3)	2.505(5)	155(4)
O^{w1}–H^{1w1}···O^{1b}	0.91(2)	2.07(3)	2.967(5)	170(4)
O^{w1}–H^{2w1}···O^{13b}	0.91(2)	2.05(3)	2.951(5)	174(4)
O^{w2}–H^{1w2}···O^{4b}(*i*)	0.91(2)	2.06(3)	2.964(5)	173(4)
O^{w2}–H^{2w2}···O^{10b}(*i*)	0.91(2)	2.10(3)	2.989(5)	166(4)

[a] Symmetry transformations of the atoms: (*i*) *x*–1, *y*, *z*; (*ii*) *x* + 1, *y*, *z* .

In the structure **I** the *E*-2-phenylethenylphosphonic acid molecule (its atoms are primed) and its anion HO_3^-PCH=CHPh (unprimed) are rather similar in the geometry. The only difference is in the respective bond lengths and bond angles at the atoms P and P′. Geometric parameters (bond lengths, bond angles, and torsion angles) of these molecule and anion are close to respective parameters of the molecule of unsubstituted acid H_2O_3PCH=CHPh [1] and of its two independent anions in the crystal structure of sodium salt **II** [2].

In the crystal **I** there are intermolecular (interionic) hydrogen bonds. Their geometric parameters are listed in Table 3. With these H-bonds infinite (along *x* axis) chains of two types are formed (see the figure). The chains of the first type are composed of alternating complex $[Na(18\text{-crown-6})(H_2O)_2]^+$ cations and 18-crown-6 (b) molecules, the chains of the second type are composed of alternating molecules of the acid H_2O_3PCH=CHPh and the respective anions.

Noteworthy that in the chains of the first type a slight statistical disordering of Na^+ cations was found. We found that in the structure **I** the independent cations Na^+ occupy two positions: the main position (Na) in the cavity of 18-crown-6 ligand (a), and a very scantily occupied position (Na') in the cavity of 18-crown-6 molecule (b). The occupancies of these positions (Na and Na′) are equal to 0.957(4) and 0.043 (4), respectively.

In the crystal structure **I** all other short intermolecular (interionic) contacts except the above mentioned H-bonds are near or slightly shorter than the sum of the corresponding atomic van der Waals radii.

EXPERIMENTAL

Complex compound **I** was synthesized as follows. Sodium salt **II** [2] and 18-crown-6 ether were dissolved in 75% aqueous ethanol in 1:1 mole ratio and the mixture obtained was left for evaporation at room temperature. After several days the colorless transparent crystals of compound **I** precipitated rather unexpectedly to the vessel bottom.

Generally speaking, we expected to obtain by this procedure a complex compound with the approximate composition $[Na(18\text{-crown-6})(H_2O)_x]^+ \cdot HO_3^-PCH{=}CHPh$. However, actually we obtained another, more complicated complex compound **I**. This fact is probably due to the hydrolysis of the parent salt **II** at the prolonged storage [2] or in the process of the synthesis of complex compound **I**.

For the X-ray structural analysis we measured parameters of the crystal unit cell and the three-dimensional set of reflex intensities on an automatic diffractometer Enraf-Nonius CAD-4 (MoK_a-irradiation, graphite monochromator). The crystals **I** are monoclinic: $[Na(C_{12}H_{24}O_6)(H_2O)_2]^+ \cdot (C_8H_8O_3P)^- \cdot C_{12}H_{24}O_6 \cdot C_8H_9O_3P$, 954.88 ; *a* 8.800(2), *b* 18.779(4), *c* 14.776(3) Å, β 102.67(2)°, *V* 2382.4(9) Å^3, *Z* 2, d_{calc} 1.331 g cm^{-3}, μ(MoK_a) 1.75 cm^{-1}, space group $P2_1$.

Intensities of 4640 reflexes were measured in the reverse space quadrant ($2\theta \le 50°$) by the method of ω/2θ-scanning from the monocrystal **I** of the size 0.14 × 0.15 × 0.44 mm. After exclusion of 11 systematically extinguished reflexes and averaging the intensities of 296 pairs of equivalent reflexes 0*kl* and 0$\bar{k}l$ (R_{int} 0.026) the working array of measured F^2 *(hkl)* and s(F^2) values consisted of 4333 independent reflexes.

The structure **I** was solved by the direct method with SHELXS-97 [9] program and refined by full-matrix least-squares method relatively to F^2 with SHELXL-97 [9] program in approximation of anisotropic thermal vibrations for nonhydrogen atoms. For the refinement were used almost all reflexes in the working array [including very weak ones with $I < 2\sigma(I)$], excluding several reflexes with bad agreement of measured and calculated F^2 values.

Positions of almost all H atoms in the structure **I** were localized in the Fourier synthesis of differential electron density in the intermediate step of anisotropic refinement. Then positions of almost all H atoms in the 18-crown-6 ligand and molecule (a and b), and in anion and molecule of acid $H_2O_3PCH{=}CHPh$ (except those at the OH groups of two latter) were assigned geometrically, their coordinates and isotropic thermal parameters were calculated using a *rider* model [9], in the procedure of refinement of structure **I**. The coordinates of four H atoms of the ligand water molecules and three H atoms in the OH groups of acid $H_2O_3PCH{=}CHPh$ molecule and anion were refined by the least mean squares method with mild geometrical restrictions of DFIX [9] type for the short interatomic distances between these H atoms.

In the final step of structure **I** refinement in the differential Fourier synthesis was also revealed a noticeable peak Δρ in the center of the cavity of 18-crown-6 molecule (b). This peak was considered to be a very poorly occupied Na' position of Na^+ cation, the alternative to its main position (Na) in the cavity of 18-crown-6 ligand (a). Total occupancies of Na and Na' positions was then refined by the least mean squares method introducing one additional varied parameter [3].

For the exposed enantiomorphous crystal **I** by the least-mean-squares method was also refined parameter of absolute structure: $\chi = -0.1(1)$ [10]. In the last cycle of full-matrix refinement the absolute shifts of all 595 varied parameters of **I** were less than 0.001σ.

The final characteristics of refinement are: $R1$ 0.044 and $wR2$ 0.094 over 2650 of observed reflexes with $I \ge 2\sigma(I)$; $R1$ 0.092 and $wR2$ 0.130 over all 4333 independent reflexes; the quality factor of adjustment $S = 0.93$ (definitions of $wR2$ and S values are given in the manual [9]). In the final Fourier synthesis of differential electron density is obtained:

$$-0.26 < \Delta\rho < 0.26\ e\ Å^{-3}.$$

Final coordinates and thermal parameters of the atoms of structure **I** and complete tables of bond lengths, bond angles and other parameters are deposited in the Cambridge bank of structural data as a cif file, deposit no. 695452.

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