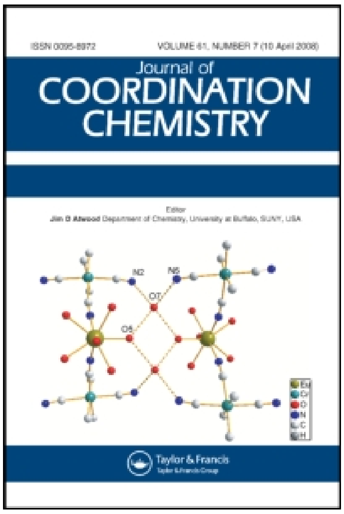

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Crystal structure of tetrasodium 5-chloro-phenylene-1,3-diphosphonate decahydrate: gutter-shaped aquatic domains for the alkali cations

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Neutralization of 5-chloro-phenylene-1,3-diphosphonic acid by sodium hydroxide in water affords quantitative yields of a tetrasodium salt as a crystalline decahydrate. The structure consists of thick uni-dimensional gutter-shaped domains in which the sodium cations are embedded in a hydrate matrix. The edges of the gutters are supported by indented stacks of anions. Within the domains of hydrated cations of the composition $[Na_4(H_2O)_{10}]^{4+}$ the inequivalent sodium cations reside in the centers of vertex-, edge- and face-sharing polyhedra, of which only one has phosphonate oxygen atoms and a chloro-substituent of the anions as donor atoms. The Cl-Na contacts and an extended hydrogen-bonding network involving all water molecules and the phosphonate groups are connecting the gutters into space-filling bundles extending along the crystallographic *c*-axis. The asymmetric units of the gutter-like realms of the cations are chiral, but both enantiomeric forms are present in the crystal and related through centers of inversion and glide planes.

Keywords: Multinuclear sodium hydrate assembly; Phenylene-1,3-diphosphonate salt; Arene stacking; Hydration of sodium cations; Aquatic domains for cations

1. Introduction

There is great current interest in the crystal engineering of ionic compounds with multifunctional cations or anions of pronounced directionality. However, more often than not the design of the connectivity patterns of the components is not a guarantee for successful construction of a specific structure. Too many strong and weak factors contribute to the overall motif of self-assembly of cations, anions and, where applicable, neutral components of solvates [1].

We have been interested in the syntheses of polyfunctional aryl*phosphines* $C_6H_n(PH_2)_{6-n}$ with various substitution patterns which allow the construction of metal complexes with one- and two-dimensional structures. Thus, 1,3,5-$C_6H_3(PH_2)_3$ is a star-

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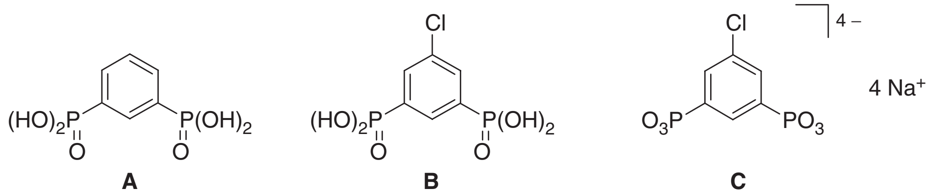
shaped trifunctional unit [2] while 1,2- and 1,3-$C_6H_4(PH_2)_2$ molecules are angular difunctional units with 60° [3] and 120° angles, respectively, and 1,4-$C_6H_4(PH_2)_2$ is a linear two-functional unit [4]. These molecules can be prepared by reduction of the corresponding aryl*phosphonates*. The aryl*phosphonic acids* serve also as polyfunctional building blocks, with their anionic charge depending on the degree of deprotonation chosen for a given construction. Their structural chemistry in many ways resembles that of the carboxylates and (hydroxy/amino)carboxylates, which have also been shown to have an extensive supramolecular chemistry [5,6].

Angular units based on the diphosphonic acid 1,3-$C_6H_4(PO_3H_2)_2$ (**A**) can be employed with additional substituents in the arene part, and *e.g.* a chlorine substituent in the 5-position has a strong influence on the polarity and polarizability of the π-system. This 5-chloro-phenylene-1,3-diphosphonic acid (**B**) can be fully deprotonated at both phosphonic acid functions by sodium hydroxide in water to give the tetra-sodium salt (**C**) in quantitative yield. This salt was found to crystallize from water at room temperature as a decahydrate [$\mathbf{C} \cdot (H_2O)_{10}$] and its crystal structure was determined showing an interesting, unprecedented array of its components. These results are described in this account and briefly discussed in the context of structures of other sodium arylphosphonates (scheme 1).



Scheme 1. Phenylene-1,3-diphosphonic acids and -phosphonates (**A**)–(**C**).

Many alkali (hydroxy/amino)carboxylates and their phosphonate analogues are generally known to be highly hygroscopic. Their ability to store large amounts of water makes certain derivatives very useful as moisturizing ingredients, applied *e.g.* in cosmetics and dermatology [7]. The water absorbed in the solids can be stored in very different, as yet unpredictable distributions. In the title compound the water molecules are attracted solely to the cations to form ‘‘aquatic’’ domains of a most peculiar one-dimensional shape.

2. Experimental

2.1 *Preparation*

The title compound was prepared by neutralization of a solution of 5-chloro-phenylene-1,3-diphosphonic acid (100.8 mg, 0.37 mmol) obtained *via* the synthetic procedure published recently from this Laboratory [2] in 10 mL of distilled water with sodium hydroxide (59.2 mg, 1.48 mmol) at room temperature. For crystal growth the flask containing a clear solution was set aside for several days at this temperature. A precipitate was obtained in quantitative yield (200.0 mg, 100%). Anal. Calcd. For $C_6H_{23}ClNa_4O_{16}P_2$(%): C, 13.33; H, 4.29; P, 11.46. Found: C, 13.24; H, 4.32; P, 11.30.

Table 1. Crystal data, data collection and structure refinement for tetrasodium 5-chloro-phenylene-1,3-diphosphonate decahydrate, $\mathbf{C}\cdot(H_2O)_{10}$.

Empirical formula	$C_6H_{23}ClNa_4O_{16}P_2$
M	540.59
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	24.9990(1)
b/Å	6.4340(1)
c/Å	25.4830(2)
$\alpha = \beta = \gamma/^\circ$	90
V/Å^3	956.43(3)
ρ_{calc}/g cm^{-3}	1.752
Z	8
$F(000)$	2224
T/K	143
Refls. measured	131810
Refls. unique	4706
Parameters/restraints	354/0
$R1$ [$I \geq 2\sigma(I)$]	0.0310
$wR2$[a]	0.0854
Weighting scheme	a = 0.0455, b = 3.7200
σ_{fin}(max/min)/eÅ^{-3}	0.378/−0.558

[a] $wR2 = \{\Sigma[w(F_o{}^2\text{-}F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$;
$w = 1/[\sigma^2(F_o{}^2)+(ap)^2+bp]$; $p = (F_o{}^2+2F_c{}^2)/3$.

2.2 *Crystal structure determination*

A crystalline specimen of the compound of suitable quality and size was mounted on the end of a quartz fiber in inert perfluoropolyalkylether and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo K_α radiation. The structure was solved by a combination of direct methods (SHELXS-97) and difference-Fourier syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97) [8]. The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were located and refined with isotropic diplacement parameters. Further information on crystal data, data collection and structure refinement is summarized in table 1.

3. Description and discussion of the structure

Crystals of the title compound are orthorhombic, space group *Pbca*, with Z = 8 formula units in the unit cell. The asymmetric unit contains four sodium cations (Na1–Na4), one 5-chloro-phenylene-1,3-diphosphonate tetraanion (with the phosphorus atoms P1 and P2 bearing the sets of oxygen atoms O11–O13 and O21–O23, respectively) and ten water molecules (with their oxygen atoms numbered O1–O10). These components and their connectivity within this unit are shown in figure 1.

It is obvious from figure 1 that in the asymmetric unit only the sodium atom Na2 has a complete octahedral coordination sphere of six water molecules, while the three other sodium atoms accept additional atoms from neighboring units as shown in figure 2. Through this coordination the atoms Na3 and Na4 – like Na2 – are also coordinated

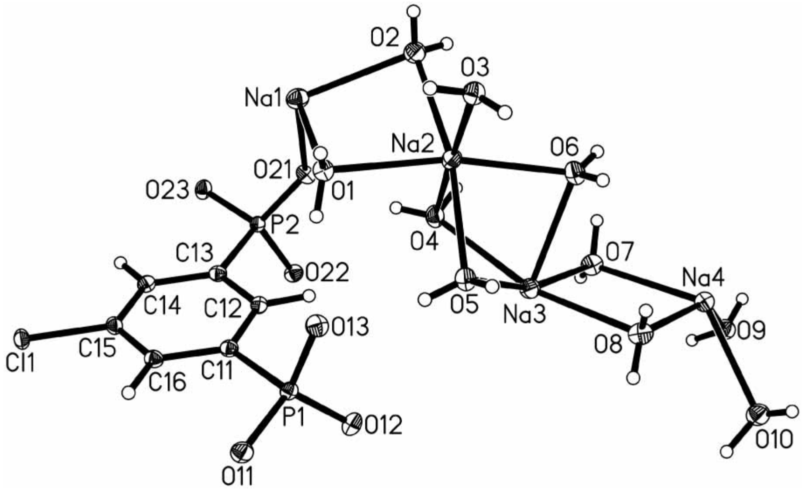


Figure 1. Asymmetric unit in the crystals of the title compound (ORTEP, 50% probability ellipsoids) with atomic numbering.

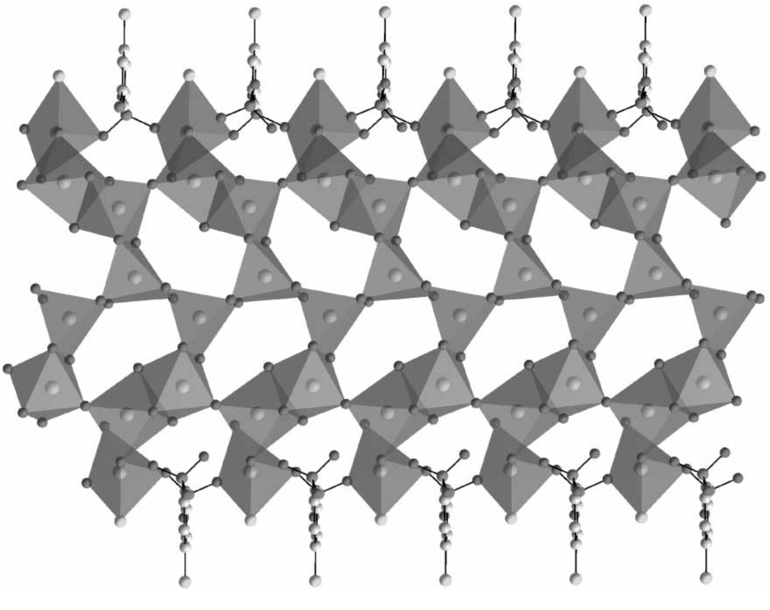


Figure 2. Projection along the crystallographic *c*-axis and perpendicular to the gutters (shaded, extending left to right) formed by vertex-, edge- and face-sharing, sodium-centered polyhedra $[Na_8(H_2O)_{20}]$ (arbitrary radii). The arene-phosphonate planes at the rims are perpendicular to the plane of the paper.

solely by (six) water molecules, which are all shared by two sodium cations. To be specific, Na4 has a trigonal prismatic environment with three edges shared with Na3, Na4′ and Na4″, while the octahedron around Na3 has a common face with Na2, a common edge with Na4 and a common vertex with Na2′. Na1 is special in that it has only coordination number 5, sharing its two water molecules at one edge with Na2 and having two vertices occupied by phosphonate oxygen atoms. Surprisingly, the fifth corner of the distorted polyhedron around Na1 is taken on by the chlorine atom of an anion of a neighboring unit at a distance of Na1–Cl1′ 3.1663(7) Å. For comparison, the Na–Cl distance in the sodium chloride crystal where sodium cations are interacting with (six) chloride anions is 2.8198 Å.

As shown in figures 2 and 3 the sodium-centered polyhedra are assembled in gutter-shaped domains. The asymmetric units associated in a given gutter are related by crystallographic glide planes, while screw axes and inversion centers relate the components of different gutters.

The two long edges of a one-dimensional sublattice component of composition $\{[Na_4(H_2O)_{10}]^{4+}\}_n$ are folded to the same side of the middle plane of the gutter and bear stacks of 5-chloro-phenylene-1,3-diphosphonate anions (figure 2). The anions are bridging two neighboring Na1 centers of the same gutter *via* one of their phosphonate groups (oxygen atoms O21 and O22), while the second phosphonate group (oxygen atoms O11–O13) is engaged only in hydrogen bonding with water molecules. The stacks of anions of neighboring gutters are indented mutually inserting their peripheral chlorine atoms into the coordination polyhedra of Na1′ centers. The projection perpendicular to the arene planes clearly shows that there is no significant overlap of the benzene rings (figure 3), and therefore no π–π stacking. However, the distances of the chlorine atom inserted between two benzene rings and the centers of these rings (3.193 and 3.250 Å) suggest weak, but significant interactions.

There is an extensive network of hydrogen bonding connecting the gutters containing the hydrated cations with the edges bearing the anions. As shown in table 2, almost without exception the O–H—O bridges always involve one phosphonate and one water oxygen atom. The O–H—O angles are all very large and the distances short indicating strong interactions.

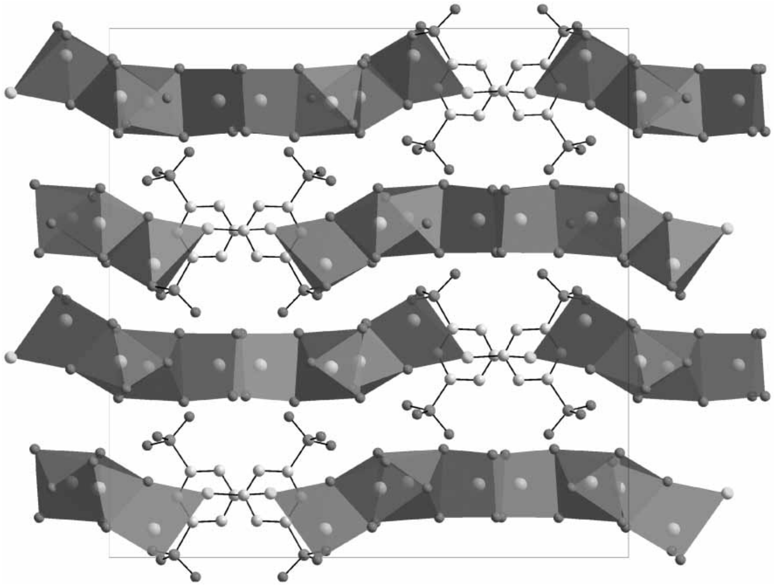


Figure 3. Projection along the crystallographic *b*-axis and parallel to the $Na_8(H_2O)_{20}$ gutters (arbitrary radii). The shaded parts represent vertex-, edge- and face-sharing, sodium-centered polyhedra.

Table 2. Hydrogen bonding in the lattice of tetrasodium 5-chloro-phenylene-1,3-diphosphonate decahydrate, $\mathbf{C}\cdot(H_2O)_{10}$.

O–H···O	d(O–H) [Å]	d(H···O) [Å]	d(O···O) [Å]	<(OHO) [°]
O(1)–H(1A)···O(12)^1	0.88(3)	1.84(3)	2.711(2)	172(3)
O(1)–H(1B)···O(13)	0.86(3)	2.09(3)	2.926(2)	166(2)
O(2)–H(2B)···O(4)^1	0.86(3)	2.19(3)	3.048(2)	177(2)
O(2)–H(2A)···O(22)^2	0.84(3)	1.89(3)	2.727(2)	170(3)
O(3)–H(3B)···O(12)^1	0.89(3)	1.92(3)	2.778(2)	163(2)
O(3)–H(3A)···O(13)^3	0.82(3)	1.95(3)	2.770(2)	176(2)
O(4)–H(4B)···O(21)^2	0.85(3)	1.93(3)	2.777(2)	176(3)
O(4)–H(4A)···O(21)	0.82(3)	1.99(3)	2.805(2)	172(3)
O(5)–H(5A)···O(13)	0.84(3)	2.04(3)	2.863(2)	167(3)
O(5)–H(5B)···O(12)^3	0.79(3)	1.97(3)	2.759(2)	178(3)
O(6)–H(6B)···O(11)^3	0.77(3)	2.06(3)	2.817(2)	168(3)
O(6)–H(6A)···O(23)^2	0.83(3)	1.99(3)	2.786(2)	160(3)
O(7)–H(7A)···O(22)^4	0.79(3)	2.02(3)	2.799(2)	167(3)
O(7)–H(7B)···O(23)^2	0.89(3)	2.19(3)	3.049(2)	160(2)
O(8)–H(8B)···O(13)^5	0.88(3)	1.98(3)	2.824(2)	162(3)
O(8)–H(8A)···O(11)^3	0.77(3)	2.10(3)	2.850(2)	163(3)
O(9)–H(9B)···O(23)^4	0.85(3)	2.02(3)	2.857(2)	165(2)
O(9)–H(9A)···O(23)^6	0.81(3)	2.09(3)	2.836(2)	153(3)
O(10)–H(10B)···O(11)^5	0.95(3)	1.74(3)	2.689(2)	173(3)

^{1}x,y−1,z; ^{2}−x+1,−y+2,−z; ^{3}−x+1,y−1/2,−z+1/2; ^{4}−x+1,−y+3,−z; ^{5}−x+1,y+1/2,−z+1/2; ^{6}x−1/2,−y+5/2,−z.

The details of the structure presented in this report have many similarities with those in structures described for other sodium phosphonate hydrates: There is generally a great tendency: (1) to integrate a large number of water molecules into the ionic crystals of sodium phosphonates, and (2) to place these water molecules in the coordination sphere of the cations with a preference over the phosphonate functions. Thus in hexasodium tris(4-phosphonatophenyl)phosphine hydrate, which has no less than 27 water molecules, $C_{18}H_{12}Na_6O_9P_4\cdot 27H_2O$, the cations are also aggregated into fully hydrated clusters, with only one of the sodium cations entertaining a Na–O(phosphonate) contact [9]. In a disodium [3-(diphenylphosphino)phenyl]phosphonate hydrate isopropanol solvate, $C_{18}H_{14}Na_2O_3P\cdot(H_2O)_{5.5}(i\mathrm{PrOH})$, the sodium cations are also arranged in one-dimensional hydrated chains with no Na–O(phosphonate) contacts [10]. Only when compounds of this type are crystallized from aqueous methanol, the phosphonate anions become engaged in sodium coordination, as in the disodium [4-(diphenylphosphino)phenyl]phosphonate trihydrate di-methanol solvate, $C_{18}H_{14}Na_2O_3P_2\cdot(H_2O)_3(MeOH)_2$ [11]. Fully hydrated sodium cations are accommodated in edge- or face-sharing octahedral or trigonal prisms, smaller coordination numbers than six being more an exception.

4. Conclusions

The structural preferences detected in crystals of sodium arylphosphonates have interesting consequences regarding the solubility and other properties of the compounds. With the cations already fully hydrated and the vertex-, edge- and face-sharing polyhedra assembled in domains surrounded by the anions with lipophilic "extremities", the salts are often poorly soluble in water. The solubility in alcohols is generally greater because these solvent molecules function as mediators between the components.

These solubility properties are of interest for the applications mentioned in the introduction. Substrates which are irreversibly hygroscopic and yet not deliquescent under ambient conditions have advantages in surface technology in general, and in dermatology and cosmetics in particular. Naturally, sodium carboxylates and (hydroxy/amino)-carboxylates, like sodium pyroglutamate or sodium lactate, are more common and have an established position in the markets [7,12], but phosphonates may offer a new variety of properties.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 247987. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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