

# Chemistry of organophosphonate scale growth inhibitors: two-dimensional, layered polymeric networks in the structure of tetrasodium 2-hydroxyethyl-amino-*bis*(methylenephosphonate)

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## Abstract

Aminomethylene phosphonates are important scale inhibitors applied in diverse areas of technology. This study adds to the existing body of information on this subject and reports the crystal and molecular structures of tetrasodium 2-hydroxyethylamino-*bis*(methylene-phosphonate) decahydrate ( $[\text{Na}_4(\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3)_2)] \cdot 10\text{H}_2\text{O}$ , 1). The crystal structure of 1 could be described as two-dimensional polymeric layered structure hydrogen bonded into a 3D supramolecular polymeric network. The structure of the tetraanion consists of a “three-arm” backbone stemming from the N atom. Two “arms” are deprotonated methylene phosphonate ( $-\text{CH}_2\text{PO}_3^{2-}$ ) moieties and the third is a hydroxyethyl ( $-\text{CH}_2\text{CH}_2\text{OH}$ ) moiety. One Na cation forms an intramolecular complex with two oxygens from separate phosphonate groups, a hydroxyl oxygen, the nitrogen and two lattice water molecules. The position of this Na cation points to a possible coordination site for Ca in a proposed Ca-HEABMP complex (HEABMP=2-hydroxyethylamino-*bis*(methylene-phosphonate)).

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**Keywords:** Metal phosphonates; Scale inhibitors; Layered structure; Hydrogen bonding

## 1. Introduction

Organic phosphonates are used extensively in several areas and applications, such as chemical water treatment for deposit prevention and control [1,2]. In medical and pharmaceutical applications, organic phosphonates are used extensively as regulators of calcium phosphate metabolism, particularly in relation to hydroxyapatite, the major inorganic constituent of bone, or treatment of calcium-related disorders [3]. In cooling water treatment programs they are used as mineral scale inhibitors [4].

The scale inhibition process in industrial cooling water is of great economical significance because of the high costs of treating undesirable results of scale formation, high cost of water in certain arid areas and losses because of shut-down of operations [5]. Schematic structures of some extensively used, “traditional” scale inhibitors together with hydroxyethylamino-*bis*(methylene-phosphonate) (HEABMP) are shown in Fig. 1.

Understanding the intimate mechanisms of scale inhibition by organic phosphonates requires a closer look at the molecular level of their possible function. Along these lines, a systematic study has been undertaken with the goal to delineate the role of phosphonates in influencing crystal growth [4]. In this report, the crystal and molecular structures of 2-hydroxyethylamino-*bis*(methylenephosphonate) decahydrate (1) as its tetrasodium salt are reported.

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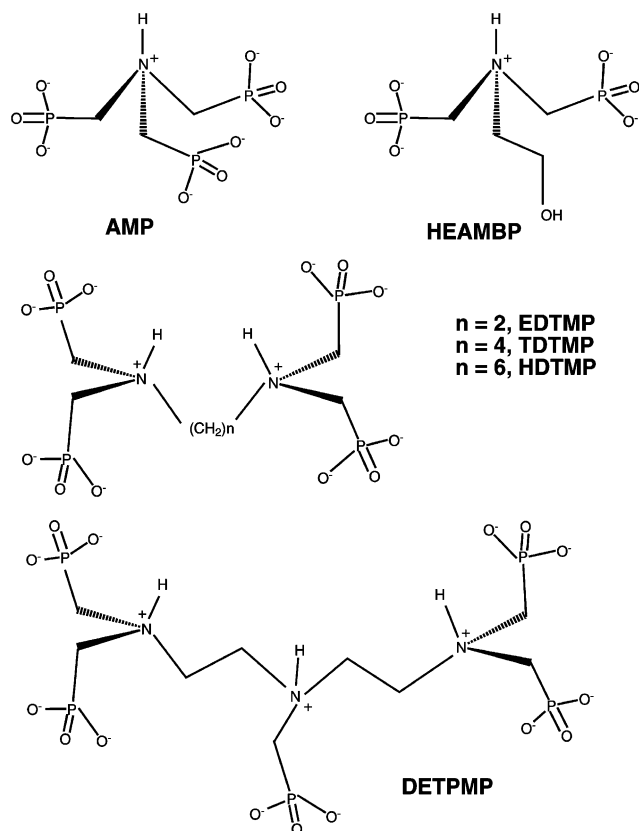


Fig. 1. Schematic structures of some representative scale inhibitors used in industrial water applications. HEAMP is highlighted in the box. Symbol abbreviations are as follows: *PBTC*: 2-phosphonobutane-1,2,4-tricarboxylic acid, *HEDP*: 1-hydroxyethylidene-1,1-diphosphonic acid, *AMP*: amino-*tris*-(methylene phosphonic acid), *HEAMP*: 2-hydroxyethyl-amino-*bis*-(methylene phosphonic acid), *EDTMP*: ethylene-diamine-*tetrakis*-(methylene-phosphonic acid), *HPAA*: hydroxyphosphono acetic acid, *DETPMP*: hexamethylenediamine-*tetrakis*-(methylene-phosphonic acid). It should be noted that all aminomethylene phosphonate molecules have the N atom protonated at pH regions below  $\sim 12$ .

## 2. Experimental section

### 2.1. Abbreviations

See legend of Fig. 1.

### 2.2. Preparations

A sample of **1** as an aqueous solution was obtained from Rhodia, Great Britain, or by literature methods [6].  $^{31}\text{P}$  NMR of the tetrasodium salt of **1** shows a singlet at 16.91 ppm (vs.  $\text{PO}_4^{3-}$ ). Single crystals of **1** as the tetrasodium salt decahydrate were obtained by slow evaporation from a concentrated solution of the compound in  $\text{H}_2\text{O}$  after standing for several weeks. The pH of the solution was  $\sim 13$ . During the crystallization process large, transparent crystals of **1** (rectan-

gular plates) formed and were isolated by filtration. They were rapidly washed with deionized water and air-dried.

### 2.3. X-ray structure determination: data collection, solution and refinement of the structure

Several regularly shaped crystals were selected and sealed in an air-tight vial (to avoid dehydration) for single crystal X-ray data collection. Relevant information concerning crystal data, intensity collection information, and structure refinement parameters for the structure are provided in Table 1. Data were collected at  $-100^\circ\text{C}$  to minimize thermal motion. Standard crystallographic methods (direct methods) were used to initially locate the heavier atoms in the structure. The remaining non-hydrogen atoms were located in subsequent difference Fourier maps. Empirical absorption corrections were applied with SADABS. The ORTEP plotting program was used to generate the structure

Table 1  
Summary of crystal data, intensity collection and structure refinement parameters for **1**

Salt	$\text{Na}_4[\text{N}(\text{CH}_2\text{PO}_3)_2(\text{CH}_2\text{CH}_2\text{OH})] \cdot 10\text{H}_2\text{O}$
Formula	$\text{Na}_4\text{C}_4\text{H}_{29}\text{P}_2\text{O}_{17}\text{N}$
Molecular weight	517.18
$a$ (Å)	6.9710(4)
$b$ (Å)	11.9607(6)
$c$ (Å)	13.1274(7)
$\alpha$ (deg)	74.761(1)
$\beta$ (deg)	89.053(1)
$\gamma$ (deg)	85.072(1)
$V$ (Å <sup>3</sup> )	1052.13(10)
$Z$	2
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	$0.30 \times 0.25 \times 0.15$
$d_{\text{calcd}}$ (g/cm <sup>3</sup> )	1.633
Diffractometer	Siemens CCD Smart
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
Collection temperature	$-100^\circ\text{C}$
Absorption coefficient $\mu$ (cm <sup>-1</sup> )	0.36
$F(000)$	539.90
$2\theta_{\text{max}}$ (deg)	60.0
Total reflections	14 186
Unique reflections	5886
Refined reflections ( $I_{\text{net}} > 2.5\sigma I_{\text{net}}$ )	4762
Merging $R$ value	0.025
Number of parameters	373
$R$ (%) <sup>a</sup> ( $R$ (%), all reflections)	2.1 (2.8)
$R_w$ (%) <sup>b</sup> ( $R_w$ (%), all reflections)	2.6 (7.7)
Goodness of Fit <sup>c</sup>	1.06
Deepest hole (e/Å <sup>3</sup> )	-0.340
Highest peak (e/Å <sup>3</sup> )	0.390

<sup>a</sup>  $R = \sum(|F_o - F_c|) / \sum F_o$ .

<sup>b</sup>  $R_w = [\sum(w|F_o - F_c|)^2 / \sum w(F_o)^2]^{1/2}$ .

<sup>c</sup>  $\text{GoF} = [\sum w(F_o - F_c)^2 / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}$ .

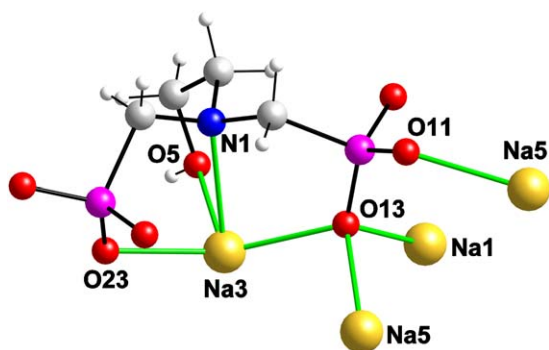


Fig. 2. ORTEP diagram (50% ellipsoids) showing symmetry independent part of **1** (upper part) and “ball and stick” representation showing a coordination mode of HEABMP tetraanionic ligand. (lower part).

shown in Fig. 2 [7]. All atoms were refined anisotropically. Hydrogen atoms were also refined. All computations were performed by using the NRCVAX suite of programs [8]. Atomic scattering factors were taken from a standard source [9] and corrected for anomalous dispersion.

The crystal of **1** contains 10 H<sub>2</sub>O molecules *per* asymmetric unit. Final positional parameters, along with their standard deviations as estimates from the inverse matrix are given in Table 2. Bond distances in **1** are given in Table 3. Tables with bond angles and torsion angles have been deposited as Supplementary Material.

#### 2.4. Instruments

For diffractometer details, see Table 1. IR spectra were recorded on a FT-IR Perkin–Elmer FT 1760.

### 3. Results and discussion

#### 3.1. Crystal structure and lattice

Crystal data, intensity collection and structure refinement parameters are shown in Table 1. Assignment of  $P\bar{1}$  as the correct space group was verified by successful refinement of the structure in this space group. Final residual values ( $R$  and  $R_w$ , see Table 1) were satisfactory. There are no discrete molecular units of **1**. Instead, **1** participates in an intricate network of *intermolecular* and *intramolecular* interactions involving Na atoms and hydrogen bonds.

The crystal structure of **1** could be described as two-dimensional polymeric layered structure hydrogen bonded into a 3D supramolecular polymeric network. Symmetry independent part of **1** and the coordination mode of the HEABMP tetraanion are shown in Fig. 2. Its structure consists of a “three-arm” backbone stemming from the N atom. Two “arms” are fully

Table 2  
Atomic parameters  $x$ ,  $y$ ,  $z$  and  $B_{\text{iso}}$  for **1**

Atom	$x$	$y$	$z$	$B_{\text{iso}}$
Na1	0	0	0	1.87 (3)
Na2	$\frac{1}{2}$	0	$\frac{1}{2}$	2.12 (3)
Na3	0.06386(7)	0.32948 (4)	−0.10240 (4)	1.412(18)
Na4	0.25405(7)	0.18365 (4)	0.28885 (4)	1.584(20)
Na5	0.42037(7)	0.14126 (4)	0.05719 (4)	1.515(18)
P1	0.29313(4)	0.108593(24)	−0.183026(23)	0.978(10)
P2	0.28407(4)	0.535764(24)	−0.251489(23)	1.003(11)
N1	0.16439(13)	0.33679 (8)	−0.29243 (7)	1.05 (4)
C1	0.32718(17)	0.24733 (9)	−0.27994 (9)	1.10 (4)
C2	0.22319(18)	0.45420 (10)	−0.34461 (9)	1.24 (4)
C3	0.00082(17)	0.30759 (11)	−0.34666 (10)	1.38 (4)
C4	−0.18675(18)	0.37232 (11)	−0.32701 (10)	1.63 (4)
O5	−0.22339(13)	0.34321 (8)	−0.21641 (7)	1.62 (3)
O11	0.50296(12)	−0.04649 (7)	0.16877 (6)	1.32 (3)
O12	0.15834(12)	0.03849 (7)	−0.22841 (7)	1.40 (3)
O13	0.21409(12)	0.13794 (7)	−0.08419 (6)	1.26 (3)
O21	0.47370(11)	0.48054 (7)	−0.19624 (7)	1.36 (3)
O22	0.30061(12)	0.66026 (7)	−0.31692 (7)	1.49 (3)
O23	0.12036(12)	0.52515 (7)	−0.17198 (7)	1.30 (3)
O31	−0.01748(14)	0.17506 (9)	0.40447 (8)	1.86 (4)
O32	0.24368(15)	0.37512 (8)	0.18991 (8)	1.79 (4)
O33	0.09008(14)	0.13185 (9)	0.14880 (8)	1.77 (4)
O34	0.32609(16)	−0.02547 (8)	0.34982 (8)	1.96 (4)
O35	−0.14285(15)	0.33417 (9)	0.03903 (8)	1.77 (4)
O36	0.80666(14)	−0.03021 (8)	0.42657 (8)	1.75 (4)
O37	0.57666(14)	0.17496 (9)	0.21222 (7)	1.65 (4)
O38	0.44310(16)	0.21072 (9)	0.43131 (8)	2.13 (4)
O39	0.39704(21)	0.34144 (9)	0.00070 (9)	3.14 (5)
O40	−0.27572(14)	0.13335 (8)	−0.05437 (8)	1.72 (3)
H1a	0.4450 (19)	0.2747(11)	−0.2533(10)	0.96 (25)
H1b	0.3684 (21)	0.2349(12)	−0.3490(12)	2.0(3)
H2a	0.1177 (21)	0.4982(13)	−0.3851(12)	1.8(3)
H2b	0.3290 (21)	0.4516(12)	−0.3940(11)	1.7(3)
H3a	−0.0132 (19)	0.2210(12)	−0.3182(11)	1.5(3)
H3b	0.0258 (21)	0.3216(13)	−0.4268(12)	2.1(3)
H4a	−0.1823 (21)	0.4574(13)	−0.3507(12)	2.2(3)
H4b	−0.2960 (20)	0.3503(11)	−0.3646(11)	1.4(3)
H5	−0.316(3)	0.3803(15)	−0.2085(14)	3.3(4)
H31a	−0.093(3)	0.2330(17)	0.3797(14)	3.4(4)
H31b	−0.075(3)	0.1191(17)	0.4101(15)	3.6(4)
H32a	0.326(3)	0.4191(15)	0.1977(13)	2.9(4)
H32b	0.150(3)	0.4063(16)	0.1896(14)	3.3(4)
H33a	0.011(3)	0.1862(19)	0.1228(17)	4.9(5)
H33b	0.027(3)	0.0835(16)	0.1745(14)	2.9(4)
H34a	0.379(3)	−0.0378(16)	0.2952(16)	3.9(4)
H34b	0.236(3)	−0.0615(18)	0.3568(16)	4.5(5)
H35a	−0.243(3)	0.3275(17)	0.0360(16)	3.7(5)
H35b	−0.134(3)	0.3820(16)	0.0738(14)	3.3(4)
H36a	0.870(3)	−0.0820(16)	0.4643(14)	3.3(4)
H36b	0.825(3)	−0.0392(15)	0.3640(15)	3.3(4)
H37a	0.6257(25)	0.2228(15)	0.2301(13)	2.7(4)
H37b	0.646(3)	0.1197(17)	0.2202(15)	3.8(5)
H38a	0.394(4)	0.2444(21)	0.4676(20)	6.6(7)
H38b	0.516(3)	0.2586(15)	0.3995(14)	3.0(4)
H39a	0.350(3)	0.3696(17)	0.0431(17)	4.1(5)
H39b	0.424(3)	0.3926(16)	−0.0520(15)	3.5(4)
H40a	−0.257(3)	0.1919(17)	−0.0975(15)	3.9(5)
H40b	−0.336(3)	0.0999(15)	−0.0932(14)	3.4(4)

Estimated standard deviations (esd's) refer to the last digit shown. <sup>a</sup> $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid

Table 3  
Selected bond distances (Å) in **1**

Na(1)–Na(5)	3.6872(5)
Na(1)–Na(5)a	3.6872(5)
Na(1)–O(13)	2.3623(8)
Na(1)–O(13)a	2.3623(8)
Na(1)–O(40)	2.3807(9)
Na(1)–O(40)a	2.3807(9)
Na(2)–Na(4)	3.4288(5)
Na(2)–Na(4)b	3.4288(5)
Na(2)–O(34)	2.4305(11)
Na(2)–O(34)b	2.4305(11)
Na(2)–O(36)	2.3690(10)
Na(2)–O(36)b	2.3690(10)
Na(2)–O(38)	2.4429(11)
Na(2)–O(38)b	2.4429(11)
Na(3)–Na(5)	3.5164(7)
Na(3)–N(1)	2.5613(11)
Na(3)–O(5)	2.4880(10)
Na(3)–O(13)	2.3897(9)
Na(3)–O(23)	2.3430(9)
Na(3)–O(35)	2.3407(11)
Na(3)–O(39)	2.7403(15)
Na(4)–Na(5)	3.3827(7)
Na(4)–O(31)	2.3986(11)
Na(4)–O(32)	2.3125(11)
Na(4)–O(33)	2.4208(11)
Na(4)–O(34)	2.4278(11)
Na(4)–O(37)	2.4537(11)
Na(4)–O(38)	2.4108(12)
Na(4)–H(32b)	2.682(18)
Na(5)–O(11)	2.3656(9)
Na(5)–O(13)	2.3772(9)
Na(5)–O(33)	2.5773(11)
Na(5)–O(37)	2.4640(11)
Na(5)–O(39)	2.3049(11)
Na(5)–O(40)c	2.5647(11)
Na(5)–H(37b)	2.622(19)
Na(5)–H(39a)	2.691(20)
P(1)–C(1)	1.8375(11)
P(1)–O(11)d	1.5368(8)
P(1)–O(12)	1.5354(9)
P(1)–O(13)	1.5141(8)
N(1)–C(2)	1.4809(14)
P(2)–C(2)	1.8279(12)
P(2)–O(21)	1.5296(8)
P(2)–O(22)	1.5239(8)
P(2)–O(23)	1.5244(9)
N(1)–C(1)	1.4713(14)
N(1)–C(3)	1.4680(15)
C(3)–C(4)	1.5151(17)
C(4)–O(5)	1.4254(6)
O(11)–P(1)d	1.5368(8)

deprotonated methylene phosphonate ( $-\text{CH}_2\text{PO}_3^{2-}$ ) moieties and the third is a hydroxyethyl ( $-\text{CH}_2\text{CH}_2\text{OH}$ ) moiety. One of the methylene phosphonate arms uses only one oxygen donor atom (O23) to coordinate terminally to Na3 atom. The other arm uses two O donors (O11 and O13) to coordinate four Na cations. Donor O11 acts as monodentate and terminally coordinates Na5 from the adjacent formula unit, while

O13 is triply bridging Na1, Na3 and Na5 with very similar Na–O distances. O5 atom of the hydroxyethyl arm and the N1 atom are involved in the coordination of Na3. HEABMP tetraanion acts in **1** as a heptadentate chelate and concurrently as bridging ligand, which forms three five-membered metallocycles ( $-\text{O}23-\text{P}2-\text{C}2-\text{N}1-\text{Na}3-$ ,  $-\text{O}5-\text{C}4-\text{C}3-\text{N}1-\text{Na}3-$  and  $-\text{O}13-\text{P}1-\text{C}1-\text{N}1-\text{Na}3-$ ) all involving Na3. Detailed discussion of important geometrical aspects of HEABMP tetraanion coordination is warranted. Such discussion follows the general description of the crystal structure of **1** below. The role of water molecules is to mediate interactions between  $\text{Na}^+$  forming a 2D polymeric sheet-like structure (Fig. 3). Interactions between water molecules and  $\text{Na}^+$  need to be discussed in more depth in order to understand the complexity of the structure.

### 3.2. Coordination environment of Na cations

The Na–Na distances are very long and range from 3.3827(7) to 3.6872(5) Å. There are four Na cations per molecule of **1**. They participate in various modes of coordination, such as the oxygen atoms of the  $\text{PO}_3$  groups, several water molecules, the N atom and the hydroxy group of the “ethanol” portion of **1**. Figures with the coordination environments of all Na atoms have been deposited as Supplementary Material.

#### 3.2.1. Na3

The coordination sphere of Na3, partially described in the previous paragraph, is completed by two water molecules. One of them (O35) is terminal, while O39 makes a bridge between Na3 and Na5. Na–O distance for bridging O39 (2.7403(15) Å) is much longer than the one (2.3407(11) Å) for terminal O35 water. Na–O( $\text{PO}_3$ ) interactions are 2.3897(9) and 2.3430(9) Å. The Na–O(OH) interaction is 2.4880(10) Å, whereas Na–N is 2.5613(11) Å. Na3 is located in a highly distorted octahedral environment. This becomes evident by examining the N1–Na3–O angles:  $\angle \text{N}1-\text{Na}3-\text{O}5 = 69.20(3)^\circ$ ,  $\angle \text{N}1-\text{Na}3-\text{O}13 = 77.98(3)^\circ$ ,  $\angle \text{N}1-\text{Na}3-\text{O}23 = 77.28(3)^\circ$ ,  $\angle \text{N}1-\text{Na}3-\text{O}35 = 157.96(4)^\circ$ ,  $\angle \text{N}1-\text{Na}3-\text{O}39 = 105.31(4)^\circ$ . This is certainly imposed by the geometric constraints of HEABMP acting as a tetradentate ligand for Na3.

#### 3.2.2. Na5

Na5 is “nested” in an octahedral environment formed by four  $\text{H}_2\text{O}$  lattice molecules and two O atoms from  $\text{PO}_3$  groups, coming from adjacent molecules. Na–O( $\text{H}_2\text{O}$ ) interactions (all of them of bridging origin) are in the range of 2.3049(11)–2.5773(15) Å. Na–O( $\text{PO}_3$ ) interactions are 2.3656(9) and 2.3772(9) Å. O33 and O37 provide bridges between Na5 and Na4, stretching the structure along a diagonal, while O40 makes a bridge

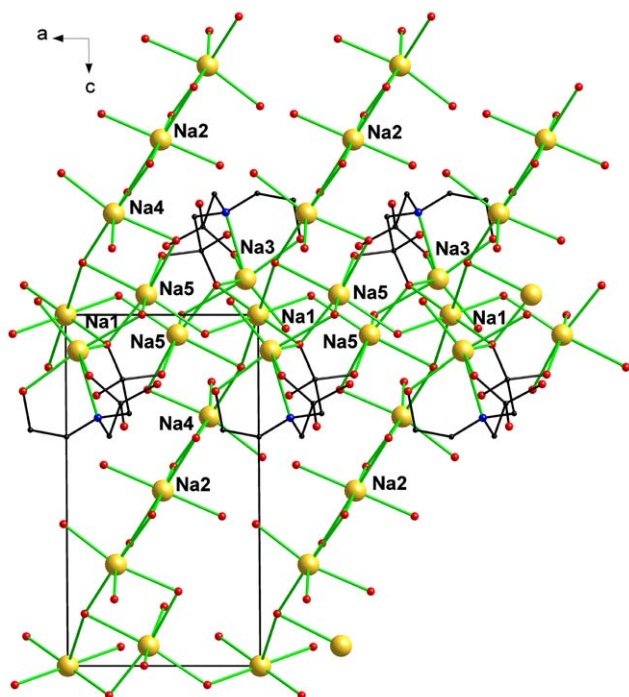


Fig. 3. Packing diagram showing 2D polymeric structure propagating in direction of both axes, *a* and *c*. Hydrogen atoms are omitted for clarity.

between Na5 and Na1 propagating the structure along the *b*-axis.

### 3.2.3. Na4 and Na2

These two cations are coordinated exclusively by water molecules. O34 and O38 atoms link them mutually via Na–O–Na bridges with Na–O bond lengths falling in the range 2.4108(12)–2.4429(11) Å. Three terminally coordinated water molecules complete their slightly distorted octahedral coordination spheres at distances spanning the range 2.3125(11)–2.3986(11) Å.

### 3.2.4. Na1

Na1 is found in highly elongated tetragonal bipyramidal coordination environment with equatorial Na–O distances 2.3623(8) and 2.3807(9) Å, and a very long axial Na1–O33 contact at 2.920(2) Å, which would be probably better described as a weak interaction rather than a coordination bond. However, this cannot be ignored as O33 is localized in the approximate apical position above the Na1 tetragonal basal plane ( $\angle$  O33–Na1–O13 = 72.30(3)°,  $\angle$  O33–Na1–O40 = 88.41(3)°). Na1 could be considered as a “nozzle” linking in a *z*-axis direction diagonally propagating zig-zag chains (–Na3–Na5–Na4–Na2–Na4–Na5–Na3–) into 2D polymeric sheets which are parallel to *ac* faces. Using this kind of terminology, the tetraanion of HEABMP acts as “protecting elbow” protruding from 2D polymeric sheet and preventing direct links between layers

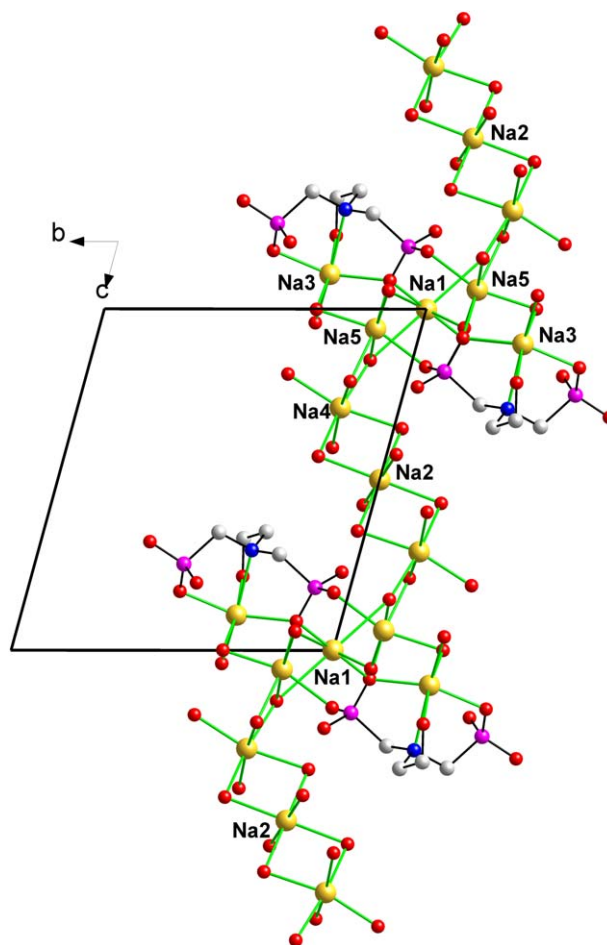


Fig. 4. Packing diagram showing a side view of 2D polymeric structure as it propagates along the *c*-axis. Hydrogen atoms are omitted for clarity.

(Fig. 4). However, these are linked via an extensive inter-layer hydrogen bond system (Table 4). Some of the hydrogen bonds are rather weak. This is inferred from the observation that the crystal lattice gradually loses water upon standing in air for a prolonged period of time and the crystal surface becomes amorphous.

### 3.3. Environment of PO<sub>3</sub> groups and the N atom

Both phosphonate groups in HEABMP are fully deprotonated. P–O bond lengths are nearly equivalent in both groups showing rather minor differences, and range from 1.5141(8) to 1.5368(8) Å. P–O bond length equivalency implies even distribution of the negative charge over all three oxygens per –PO<sub>3</sub> group. P–C bond lengths fall in the normal range (1.8–1.9 Å) and are 1.8375(11) Å and 1.8279(12) Å.

The N atom is not protonated as expected due to the high pH of crystal preparation. It forms a rather long interaction of 2.5613(11) Å with Na(3). N–C bond lengths are 1.4713(14) and 1.4809(14) Å for the methylene phosphonate “arms” and 1.4680(15) Å for the

Table 4  
Hydrogen bonds

D–H–A	D–H	H–A	D–A	<D–H–A	Symmetry operation
O40–H40a–O5	0.80	2.08	2.878(2)	176.1	$x, y, z$
O40–H40b–O11	0.86	1.80	2.651(2)	168.8	$-x, -y, -z$
O34–H34a–O11	0.84	1.88	2.720(2)	173.2	$x, y, z$
O33–H33b–O12	0.76	2.01	2.769(2)	173.8	$-x, -y, -z$
O36–H36b–O12	0.86	1.78	2.636(1)	171.7	$x, y, 1+z$
O39–H39b–O21	0.83	1.95	2.754(2)	164.1	$x, y, z$
O5–H5–O21	0.77	1.85	2.616(2)	174.8	$-1+x, y, z$
O32–H32a–O21	0.84	1.92	2.745(2)	172.0	$-1+x, y, z$
O37–H37a–O22	0.78	2.12	2.874(2)	162.6	$x, y, z$
O38–H38b–O22	0.82	1.84	2.645(2)	167.7	$x, y, z$
O31–H31a–O22	0.83	1.89	2.704(2)	166.9	$-1+x, y, z$
O32–H32b–O23	0.72	1.98	2.696(2)	169.7	$x, y, z$
O35–H35b–O23	0.83	1.92	2.739(2)	171.7	$-x, 1-y, -z$
O36–H36a–O31	0.79	2.03	2.780(2)	159.0	$x, y, z$
O39–H39a–O32	0.78	2.07	2.800(2)	156.8	$-x, 1-y, -z$
O33–H33a–O35	0.82	2.05	2.853(2)	168.7	$x, y, z$
O31–H31b–O36	0.80	1.99	2.783(2)	174.2	$-x, -y, 1-z$

“ethanol arm”. The  $\angle$  C–N–C are  $\sim 111^\circ$  and  $\angle$  Na3–N–C are 103.78(7), 109.16(7) and 108.10(7)°.

### 3.4. Structural chemistry of metal-polyphosphonates

Crystal structures of *mono*-phosphinates [10] and *mono*-phosphonates [11] have been reported. In addition, an extensive number of structures of *bis* phosphonates exist [12,13] as well as *ab initio* studies on relevant organo-phosphorous compounds and their Ca complexes [14].

The crystal structure of disodium dichloro-methylene diphosphonate shows that the Na cations interact with phosphonate oxygens, the chlorine substituent and water oxygens. There is also extensive hydrogen bonding network that supports the 3D structure built by the phosphonate oxygens that bridge Na cations [13b].

AMP (Fig. 1) is conceptually a closely related phosphonate to HEAMBMP in that one  $-\text{CH}_2\text{PO}_3\text{H}_2$  group in the former is replaced by a  $-\text{CH}_2\text{CH}_2\text{OH}$  group in the latter. This change has a profound effect on the calcium tolerance (defined as the ability of an inhibitor to remain soluble in the presence of  $\text{Ca}^{2+}$ ) of the two compounds. According to preliminary studies [4d], as little as 15 ppm of AMP result in formation of Ca precipitates when added to a solution of 1000 ppm Ca, as  $\text{CaCO}_3$ . This is in direct contrast with calcium tolerance results obtained on HEAMBMP. A possible Ca–HEAMBMP complex does not precipitate even at concentrations of 300,000 ppm of  $\text{Ca}^{2+}$  and  $\sim 200,000$  ppm of HEAMBMP. Apparently, the presence of a  $-\text{CH}_2\text{CH}_2\text{OH}$  group in HEAMBMP is the source for this high calcium tolerance. Its origin could be a weak Ca–O(H) bond, much weaker than a Ca–O( $\text{PO}_3$ ) bond.

Suitable crystals for X-ray crystallography of a Ca–HEAMBMP complex have not yet been obtained. Consequently, geometric data on the Ca–HEAMBMP complex are not available. However, one can extrapolate results from the present study in the following manner. Intramolecular Na–O( $\text{PO}_3$ ) bond lengths are 2.3897(9) and 2.3430(9) Å in **1**. The Na–O(H) bond length is 2.4880(10) Å,  $\sim 0.1$  Å longer than the Na–O( $\text{PO}_3$ ) bond lengths. It is reasonable to propose that a similar bond length distribution will be likely found in a possible Ca–HEAMBMP complex, with the Ca–O(H) bond being longer and weaker than the Ca–O( $\text{PO}_3$ ) bonds.

These assumptions are substantiated in the structure of a Ca–HEDP complex. Intramolecular Ca–O( $\text{PO}_3$ ) bond distances are 2.352(4) and 2.420(3) Å, whereas the Ca–O(H) bond is much longer, at 2.608(3) Å [13a]. In addition, similar observations can be made for a corresponding Rb–HEDP complex. Intramolecular Rb–O( $\text{PO}_3$ ) bond distances are 2.949(3) and 2.952(3) Å, whereas the Rb–O(H) distance is much longer, at 3.078(3) Å [15].

Structures of metal-aminomethylene-phosphonates have been reported by various research groups. From the vast literature we only refer to some representative examples. These include divalent metals with AMP, such as Mn–AMP [16], Pb–AMP [17], Cd–AMP [18], Ca–AMP [4b,19] and alkaline metals, such as Na–AMP [20]. Also, structures of metal-tetraphosphonates having the two amino-*bis*-methylene phosphonates moieties separated by long carbon chains have appeared in the literature. For example,  $\text{Ca}[(\text{HO}_3\text{PCH}_2)_2\text{N}(\text{H})-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-\text{N}(\text{H})(\text{CH}_2\text{PO}_3\text{H})_2] \cdot 2\text{H}_2\text{O}$  is a microporous material [21]. A similar compound with a shorter carbon chain between the N atoms,  $\text{Mn}[(\text{HO}_3\text{PCH}_2)_2\text{N}(\text{H})-(\text{CH}_2)_4-\text{N}(\text{H})(\text{CH}_2\text{PO}_3\text{H})_2]$ , was also reported [22]. Trivalent metal polyphosphonates e.g. Al–AMP have also been described [23]. The compound  $\text{Na}_2[(\text{HO}_3\text{PCH}_2)_3\text{NH}] \cdot 1.5\text{H}_2\text{O}$  [20] is formed between Na cations and an AMP triphosphonate. The triphosphonate has an overall charge of “-2-”, due to the presence of three singly deprotonated phosphonate groups and the protonated N. The latter is not coordinated to  $\text{Na}^+$ . Therefore, direct comparisons between **1** and  $\text{Na}_2[(\text{HO}_3\text{PCH}_2)_3\text{NH}] \cdot 1.5\text{H}_2\text{O}$  can only be limited to Na–O distances, which are rather similar.

An important structural feature common in essentially all metal-aminomethylene-phosphonate structures is the coordination of the metal center by the phosphonate O's and not by the N moiety. This is expected because N is protonated at the pH region of synthesis. It is not the case with HEAMBMP. Its crystals are prepared at sufficiently high pH's rendering the N deprotonated, and thus, available for coordination. Another feature common in these metal-phosphonates is the bridging ability of phosphonate O's. This

phenomenon is also observed in the present structure, where triply bridging phosphonate O's are observed.

Complex formation equilibria studies of amino polyphosphonates can also be found in the literature [24]. More specifically, Sawada et al. reported studies on complex formation of amino polyphosphonates [25]. They suggested that AMP coordinates to alkaline earth metal ions in a *tetradentate* fashion, through three phosphoryl oxygens (originating from three different PO<sub>3</sub> groups) and the central nitrogen. This is similar to the fashion one of the Na cations resides in the “coordination cavity” in **1** (see Fig. 2). We have performed our own <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR studies (results to be published) to study solution interactions of HEAMBP with Ca<sup>2+</sup>. We have discovered that the phosphonate oxygens are the preferred sites for Ca<sup>2+</sup> coordination. N may play a role in coordination with Ca<sup>2+</sup> only when it is deprotonated at pH regions > 12.

Structural studies on metal amino-methylenephosphonates with N participation in coordination are scarce in the literature. This is because syntheses and growth of appropriate crystals need to be carried out in high pH regions, so the N–H<sup>+</sup> moiety is deprotonated. Unfortunately, such metal phosphonates (particularly, those containing alkaline earth cations) are extremely insoluble and form amorphous materials at high pH's.

### 3.5. Vibrational analysis

An FT-IR spectrum of **1** shows an intense peak centered at 3440 that is assigned to the O–H stretch of the waters of crystallization. Its intensity is explained by the presence of 10 water molecules of crystallization. A lower intensity band at 1643 is assigned to ν<sub>2</sub> bend of H-bonded H<sub>2</sub>O. Another intense band at 1078 is due to the antisymmetric stretch of PO<sub>3</sub> groups. Finally, a medium-size intensity band at 966 could be due to the P–O stretch, whereas a weak peak at 580 could be due to PO<sub>3</sub> bend. The FT-IT spectrum of **1** has been deposited as Supplementary Material.

## 4. Conclusions/perspectives

The principal findings of this study are summarized below.

1. The molecular structure of **1** reveals that a Na cation resides in a peculiar “pocket” shaped by two phosphonate oxygens, the hydroxyl oxygen and the nitrogen. This site could be a possible coordination environment for other cations of interest, such as Ca<sup>2+</sup>.
2. There is extensive hydrogen bonding in the crystal lattice. Both phosphonate groups are *fully* deprotonated. However, the hydroxyl group is found to be protonated.

Metal-phosphonate chemistry is an important field of research [26]. Phosphonic acids have attracted significant attention due to their utility in supramolecular chemistry and crystal engineering [27]. Metal-phosphonates commonly form pillared-layered inorganic–organic hybrid materials and microporous solids [28]. These properties can be useful for intercalation, catalysis, sorption, and ion exchange. In these architectures hydrogen bonds are predominant resulting in one-, two-, and three-dimensional supramolecular networks. We are currently interested in metal-phosphonate chemistry as this relates to chemical water treatment [4b], oilfield [29], and corrosion control applications [30]. The present study presents structural chemistry of HEAMBP. This, to our knowledge, is the only example of a structure showing a fully deprotonated amino-methylenephosphonate with all phosphonate and N participation in coordination with metal cations.

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## Appendix A. Supplementary material

Various tables and figures with structural details and an infrared spectrum of [Na<sub>4</sub>(HOCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>2</sub>PO<sub>3</sub>)<sub>2</sub>)] · 10H<sub>2</sub>O are deposited as supplementary material. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 244432. Copies of the data may be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-1223-336033, e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or <http://www/ccdc/cam/ac/uk>).

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