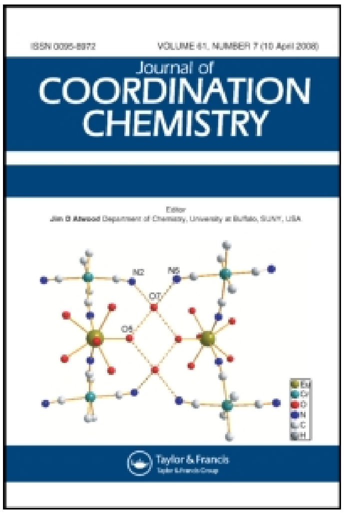

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Supramolecular hydrogen bond framework constructed by 1-aminoethylidenediphosphonic acid and monovalent ions: Li^{+}, Na^{+}, and

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Supramolecular hydrogen bond framework constructed by 1-aminoethylidenediphosphonic acid and monovalent ions: Li^+, Na^+, NH_4^+ and $(CH_3)_2NH_2^+$

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Four new monovalent 1-aminoethylidenediphosphonates, $[Li(AEDPH_3)(H_2O)]_6$ (**1**), $Na_2(AEDPH_3)_2(H_2O)_8$ (**2**), $(NH_4)(AEDPH_3)$ (**3**) and $((CH_3)_2NH_2)(AEDPH_3)(H_2O)$ (**4**) have been synthesized and characterized by elemental analysis, IR, TG together with X-ray single crystal diffraction analysis. Compound **1** is a 24-metallacrown-6 lithium structure, compound **2** is binuclear Na^+ bridged by water molecules, and compounds **3** and **4** are proton-transfer salts. All four compounds are further extended to form three-dimensional (3D) supramolecular structures with the aid of water molecules (excluding **3**) via various predictable hydrogen bonds.

Keywords: Monovalent; 1-Aminoethylidenediphosphonate; Hydrogen bonds; Crystal structure; Supramolecular

1. Introduction

Metal organophosphonates have been studied widely in the past two decades [1–4]. As a new class of organic–inorganic hydrid materials, phosphonates have potential applications in catalysis, sensors, sorbents, magnetic and luminescent materials [5–8]. Research is directed to the synthesis, structures and properties of divalent, trivalent, and pentavalent metal phosphonates. However, little attention has been focused on monovalent phosphonates [9–12]. There are several examples of phosphonates containing alkaline cations, such as $Na_2[(HO_3PCH_2)_3NH] \cdot 1.5H_2O$ [9], $Na_2[(HO_3PCH_2)NC_4H_8N(CH_2PO_3H)](H_2O)_8 \cdot 2H_2O$ [11] $A(HO_3PC_6H_5)(H_2O_3PC_6H_5)$ and $[A\{HO_3P(CH_2)_2PO_3H_2\}]$ (A = alkaline metal, NH_4) [10, 12]. In addition, compounds of 1-aminoethylidenediphosphonic acid ($AEDPH_4$) are little reported [13] with only two structural studies on the Co and Cu compounds reported recently [14]. $AEDPH_4$ transfers one proton to the amino group and exists as a zwitterion. Deprotonization results in predictable hydrogen aggregations from stronger P–O–H $\cdots$ O–P to weaker C–H $\cdots$ O hydrogen bonds, which are shown in scheme 1,

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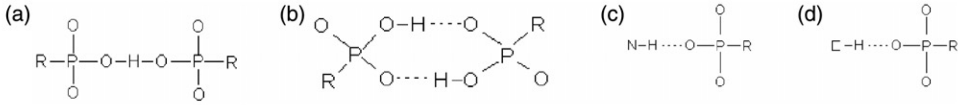

Scheme 1. Predictable hydrogen bond modes of $AEDPH_4$.

giving a chance to synthesize stable hydrogen-bonded frameworks and study how the various hydrogen bonds influence structures and properties. Herein, we describe the synthesis and characterization of four monovalent 1-aminoethylidenediphosphonates, namely, $[Li(AEDPH_3)(H_2O)]_6$ (**1**), $Na_2(AEDPH_3)_2(H_2O)_8$ (**2**), $(NH_4)(AEDPH_3)$ (**3**) and $((CH_3)_2NH_2)(AEDPH_3)(H_2O)$ (**4**).

2. Experiment

2.1. *Materials and methods*

The 1-aminoethylidenediphosphonic acid ($AEDPH_4$) was prepared according to the U. S. Patent 4239695 [15]. Other starting materials were purchased from commercial sources and used without further purification. The IR spectra were recorded with pressed KBr pellets in a range of 400–4000 cm^{-1} on a Nicolet 5700 FT-IR spectrometer with spectral resolution of 4.00 cm^{-1}. Thermogravimetric studies were carried out at a heating rate 20 K min^{-1} under air on a NETZSCH STA 449C instrument. The elemental analysis data were performed in a Perkin–Elmer 240B elemental analyzer.

2.2. *Synthesis*

Compound **1** was prepared as follows: $LiOH \cdot H_2O$ (0.0209 g, 0.5 mmol) and $AEDPH_4$ (0.1025 g, 0.5 mmol) were added in 0.25 mL H_2O in a molar ratio of 1 : 1 : 28, then the mixture was sealed and heated at 80°C; colorless crystals were obtained after 3 days. Elemental analysis (EA) Found: C 10.40, H 4.36, N 6.06; Cacld. For $C_{12}H_{60}Li_6N_6O_{42}P_{12}$: C 10.49, H 4.40, N 6.12.

Compounds **2** and **3** were synthesized by a similar method to that of compound **1** except corresponding amounts of NaOH or $NH_3 \cdot H_2O$ instead of $LiOH \cdot H_2O$, respectively. EA for **2**: Anal. C 7.99, H 5.20, N 4.79, Calcd for $C_4H_{32}N_2Na_2O_{20}P_4$: C 8.03, H 5.39, N 4.68; compound **3**: Anal. C 10.82, H 5.59, N 12.66, Calcd for $C_2H_{12}N_2O_6P_2$: C 10.82, H 5.45, N 12.62.

Compound **4** was prepared by a different procedure. $AEDPH_4$ (0.1025 g, 0.5 mmol) was added to DMF/H_2O solvent, and then the mixture was sealed and heated at 80°C. After one day, colorless crystals suitable for single crystal analysis were obtained. EA for **4**: Anal. C 17.85, H 6.65, N 10.54, Calcd for $C_4H_{18}N_2O_7P_2$: C 17.92, H 6.77, N 10.45. The dimethylammonium cation in the final product was believed to be obtained from the decomposition of DMF solvent. This has been commonly observed in hydro(solvo)thermal conditions [16–17]. The same product was also obtained by reaction with $(CH_3)_2NH$ and $AEDPH_4$ in 1 : 1 molar ratio in water.

2.3. *X-ray crystallography*

Crystallographic measurements were obtained on a Bruker SMART CCD area-detector diffractometer at room temperature (291 K) using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were corrected for absorption using the program SADABS. The structures were solved by direct methods using the program SHELXS-97 [18]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL-97. All hydrogen atoms were directly obtained from difference fourier maps. Drawings were produced with PLATON [19]. Crystallographic data and structure refinement parameters are listed in table 1. Hydrogen-bond parameters for compounds **1–4** are shown in table 2.

3. Results and discussions

3.1. *Crystal structure of 1*

Compound **1** (figure 1a) is a 24-metallacrown-6 lithium (24-Mc-6 Li) constructed from (Li–O–P–O–)$_6$ formed by Li$^+$ with oxygens in AEDPH$_3^-$. To the best of our knowledge, this is the first metallacrown containing lithium as a linker atom. Lithium ion is coordinated by three oxygen atoms of two different phosphonates and one from water molecule. The phosphonate is tridentate chelating-bridging to form a chair-structured six-member ring and links each other to construct a Li–O–P–O– ring. Each AEDPH$_3^-$ ion is coordinated to two lithium ions. The Li–O bonds range from 1.907(3) to 2.017(3) Å. Unlike other metallacrown molecules [20–21], the (Li–O–P–O–)$_6$ ring is not planar.

Hydrogen bonds between the up and down crowns of 24-Mc-6 Li, form 1D tubes along the *c* axis. Two hydrogen bonds: O(2)–H(8) $\cdots$ O(4)#7 and N(1)–H(1) $\cdots$ O(3)#4 are strong with lengths of 2.613(2) and 2.821(2) Å, respectively. The close packing pattern of 24-Mc-6 Li is ABAB fashion.

The crystal packing structure of **1** viewed along the *c* axis shows it is a three-dimensional (3D) supramolecule constructed by 24-Mc-6 Li through hydrogen bonds (figure 2b). Among the channels of three adjacent 24-Mc-6 Li, three water molecules coordinated to Li ions form an infinite helical water chain. Helical water assemblies in the water chain category are few [22–23]. The IR (the sharp bands located at 3502 cm^{-1}) also confirms the existence of water clusters [24]. The O$_w$ is tetrahedral including Li–O, a P–O $\cdots$ O$_w$ and two O$_w \cdots$ O$_w$ hydrogen bonds. The O$_w \cdots$ O$_w$ distance is 2.989 Å, longer than that of liquid water (2.85 Å) [25]. The angle of O$_w \cdots$ O$_w \cdots$ O$_w$ is 119.55°, different than the corresponding value of 109.3°. The helical water chains are fixed by the Li–O$_w$ bond and O$_w$–H $\cdots$ O–P hydrogen bond as mentioned above. The six water helices around 24-Mc-6 Li are alternately right- and left-handed (PMPMPM, P = plus or right-handed and M = minus or left-handed). A similar helical pattern has been recently reported [23].

3.2. *Crystal structure of 2*

Compound **2** crystallizes in triclinic space group $P\bar{1}$. Figure 2(a) shows the building unit of the structure with atomic labeling scheme. Clearly, it is binuclear Na$^+$ bridged by

Table 1. Crystallographic data and structure refinement for compounds **1**–**4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{60}Li_6N_6O_{42}P_{12}$	$C_4H_{32}N_2Na_2O_{20}P_4$	$C_2H_{12}N_2O_6P_2$	$C_4H_{18}N_2O_7P_2$
Formula weight	1373.94	598.18	222.08	268.14
Temperature (K)	291(2)	291(2)	291(2)	291(2)
Wavelength	0.71073	0.71073	0.71073	0.71073
Crystal system	Trigonal	Triclinic	Monoclinic	Monoclinic
Space group	R-3	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
a (Å)	24.717(3)	5.6933(5)	7.3372(5)	11.0738(6)
b (Å)	24.717(3)	8.9074(7)	10.6496(7)	6.9390(4)
c (Å)	7.2978(18)	11.9358(10)	10.6098(7)	14.4504(8)
α (°)	90	70.8600(10)		
β (°)	90	85.2350(10)	97.7020	94.0950(10)
γ (°)	120	79.3150(10)		
Volume (Å^3)	3861.1(12)	561.76(8)	821.55(9)	1107.55(11)
Z, $D_{(\mathrm{Cacld})}$ (g cm^{-3})	3, 1.773	1, 1.768	4, 1.795	4, 1.608
Absorption coefficient (min^{-1})	0.512	0.468	0.528	0.413
F(000)	2124	312	464	568
Crystal size (mm^3)	$0.38 \times 0.09 \times 0.09$	$0.92 \times 0.52 \times 0.19$	$0.46 \times 0.36 \times 0.29$	$0.45 \times 0.34 \times 0.21$
Theta range for data collection	2.85–27.98	2.46–27.00	2.72–27.50	2.24–27.50
Index ranges	$-32 \le h \le 32$, $-28 \le k \le 32$, $-8 \le l \le 9$	$-6 \le h \le 7$, $-11 \le k \le 11$, $-15 \le l \le 9$	$-8 \le h \le 9$, $-13 \le k \le 11$, $-13 \le l \le 13$	$-14 \le h \le 14$, $-9 \le k \le 8$, $-15 \le l \le 18$
Reflections collected Independent reflections/reflections observed ($>2\sigma$)	8670/2067 [R(int) = 0.0256]	3461/2379 [R(int) = 0.0122]	5188/1874 [R(int) = 0.0105]	6875/2528 [R(int) = 0.0111]
Data completeness	99.9%	96.8%	99.2%	99.6%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2067/0/158	2379/0/210	1874/0/158	2528/0/209
Goodness-of-fit on F^2	1.071	1.088	1.082	1.059
Final R indices [$I > 2\sigma(I)$]	R_1 a $= 0.0278$, wR_2 b $= 0.0740$	$R_1 = 0.0240$, $wR_2 = 0.0700$	$R_1 = 0.0234$, $wR_2 = 0.0711$	$R_1 = 0.0246$, $wR_2 = 0.0701$
R indices (all data)	$R_1 = 0.0333$, $wR_2 = 0.0781$	$R_1 = 0.0246$, $wR_2 = 0.0708$	$R_1 = 0.0241$, $wR_2 = 0.0717$	$R_1 = 0.0259$, $wR_2 = 0.0713$
Largest diff. peak and hole (e Å^{-3})	0.375 and -0.338	0.520 and -0.311	0.369 and -0.316	0.420 and -0.273

[a] $R_1 = [\Sigma(|F_o| - |F_o|)/\Sigma|F_o|$;

[b] $wR_2 = [\Sigma[w(|F_o|^2 - |F_o|^2)^2]/\Sigma[w(|F_o|^2)^2]^{1/2}$, $w = 1/[\sigma^2|F_o|^2 + (xp)^2 + yp]$; where $p = [|F_o|^2 + 2|F_o|^2]/3$.

Table 2. Hydrogen bonds parameters for **1**–**4**.

D–H···16	D···A(Å)	∠D–H···A(°)	D–H···A	D···A(Å)	∠D–H···A(°)
1[a]					
O(2)–H(8)···O(4)#7	2.613(2)	175(4)	O(5)–H(7)···O(1)#3	2.578(2)	163(3)
N(1)–H(2)···O(1)#3	2.912(2)	166(2)	N(1)–H(1)···O(3)#4	2.821(2)	163(2)
N(1)–H(3)···O(6)#1	2.762(2)	178(2)	O(1W)–H(1W1)···O(1W)#6	2.990(2)	161(3)
O(1W)–H(2W1)···O(1)#5	2.883(2)	161(3)			
2[b]					
O(3)–H(8)···O(5)#3	2.6735(15)	174(2)	O(6)–H(7)···O(4)#9	2.5593(14)	178(2)
N(1)–H(4)···O(4)#6	2.7884(14)	148.0(16)	N(1)–H(5)···O(5)#2	2.7776(15)	141.9(16)
N(1)–H(6)···O(2)#6	2.7730(14)	159.5(16)	O(1W)–H(2W1)···O(4W)#1	2.8244(18)	160(2)
O(1W)–H(1W1)···O(6)#2	3.1981(16)	126(2)	O(1W)–H(1W1)···O(5)#2	3.0267(17)	168(3)
O(2W)–H(2W2)···O(1W)#4	2.8576(19)	174(2)	O(2W)–H(1W2)···O(3)#1	3.1958(16)	126(3)
O(3W)–H(1W3)···O(1)#5	2.8423(16)	171(2)	O(3W)–H(2W3)···O(2)#6	2.8574(15)	173(2)
O(4W)–H(2W4)···O(2)#7	2.8535(16)	158(2)	O(4W)–H(1W4)···O(3W)#8	2.7943(17)	166(2)
3[c]					
O(1)–H(4)···O(4)#6	2.5462(14)	172(2)	O(6)–H(5)···O(2)#5	2.5886(15)	172(2)
N(1)–H(1N1)···O(3)#4	2.8100(14)	159.7(17)	N(1)–H(2N1)···O(5)#4	2.7138(14)	158.5(17)
N(1)–H(3N1)···O(2)#5	2.8233(14)	153.0(17)	N(2)–H(1N2)···O(5)#4	2.8047(16)	160(2)
N(2)–H(2N2)···O(4)#2	2.8181(16)	172.9(19)	N(2)–H(3N2)···O(3)#3	2.8259(17)	176(2)
N(2)–H(4N2)···O(1)	3.0564(16)	113.0(15)	N(2)–H(4N2)···O(2)#1	3.0393(16)	142.1(17)
C(2)–H(3)···O6#4	3.3822(17)	142.7(17)			
4[d]					
O(1)–H(1)···O(5)#5	2.5429(13)	175(3)	O(6)–H(2)···O(4)#6	2.5589(13)	171(3)
N(1)–H(6)···O(1)#5	2.8758(14)	161.2(17)	N(1)–H(6)···O(5)#5	3.0213(14)	115.0(14)
N(1)–H(7)···O(7W)#4	2.8651(17)	172.7(17)	N(1)–H(8)···O(3)#3	2.8300(14)	169.4(17)
N(2)–H(9)···O(3)	2.7744(16)	168(2)	N(2)–H(10)···O(2)#2	2.7794(17)	161(2)
O(7W)–H(17)···O(2)	2.7268(16)	170(2)	O(7W)–H(18)···O(4)#1	2.9555(17)	161(3)
C(2)–H(3)···O(5)	3.5550(16)	170.7(13)			

[a] Symmetry codes: #1 $x-y+1, x+1, -z$; #3 $-x+1/3, -y+5/3, -z+2/3$, #4 $x-y+1, x+1, -z+1$; #5 $-y+2/3, x-y+4/3, z-2/3$; #6 $-x+y-2/3, -x+2/3, z-1/3$; #7 $x, y, z+1$.

[b] Symmetry codes: #1 $-x, -y+3, -z$; #2 $-x, -y+2, -z+1$; #3 $-x+1, -y+2, -z+1$; #4 $-x-1, -y+3, -z$; #5 $-x, -y+2, -z$; #6 $x-1, y, z$; #7 $-x+1, -y+2, -z$; #8 $x+1, y, z$; #9 $-x+1, -y+1, -z+1$.

[c] Symmetry codes: #1 $-x+1, -y, -z$; #2 $x-1, -y+1/2, z-1/2$; #3 $-x+1, y+1/2, -z+1/2$; #4 $-x+2, y+1/2, -z+1/2$; #5 $-x+2, -y, -z$; #6 $x-1, y, z$.

[d] Symmetry codes: #1 $-x+3/2, y+1/2, -z+1/2$; #2 $x, y+1, z$; #3 $-x+1/2, y-1/2, -z+1/2$; #4 $x-1/2, -y+1/2, z-1/2$; #5 $-x+1/2, y+1/2, -z+1/2$; #6 $-x+1, -y, -z$.

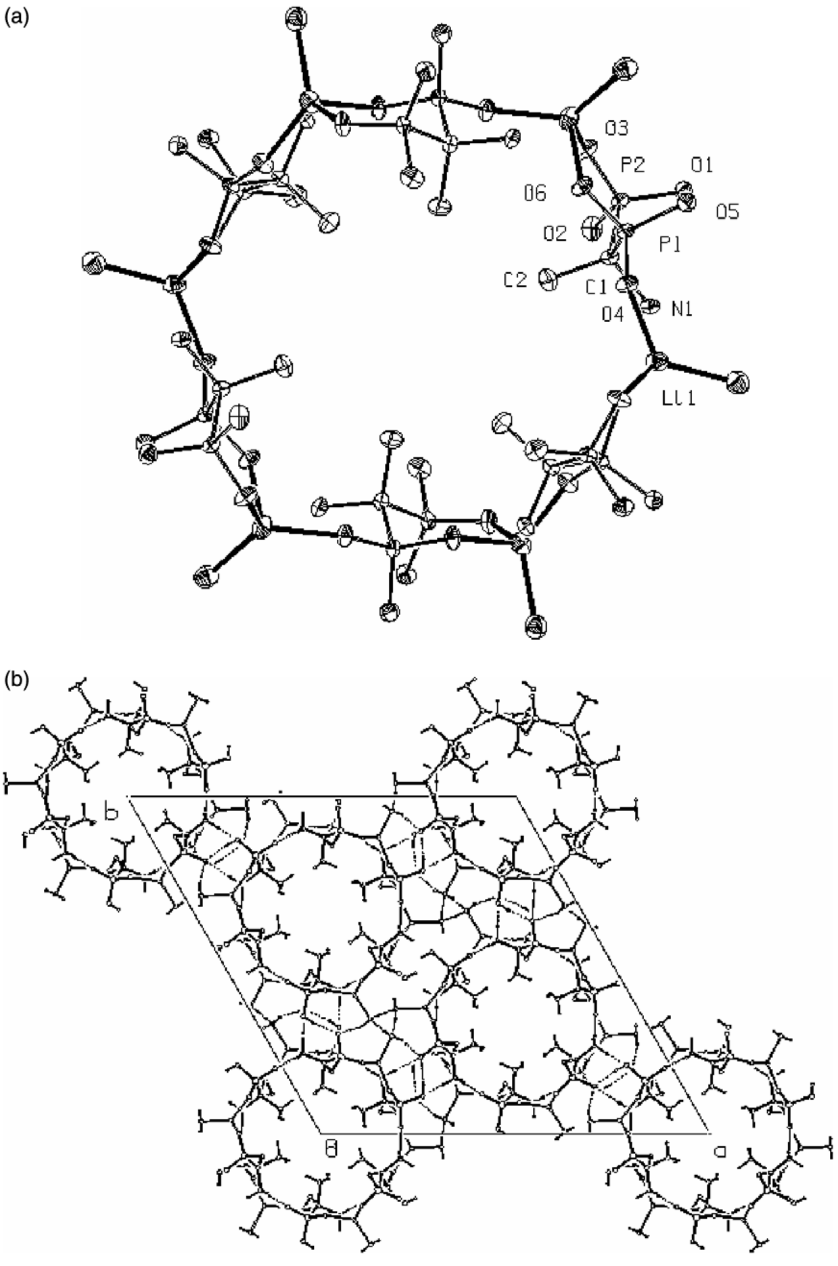

Figure 1. (a) The ORTEP of **1** with thermal ellipsoids at the 50% probability, all H atoms are omitted for clarify. (b) Crystal packing diagram of **1** viewed along the *c* axis.

water molecules. The Na^+ ion is six-coordinate by five oxygen atoms of water and one oxygen from $AEDPH_3^-$. The O2W and O2Wa act as μ_2-bridges linking two Na^+ ions and forming a Na_2O_{10} dimer. The $AEDPH_4$ deprotonates transferring to amino, which behaves as a zwitterion. Along the *bc* plane, the $AEDPH_3^-$ anions link each other to

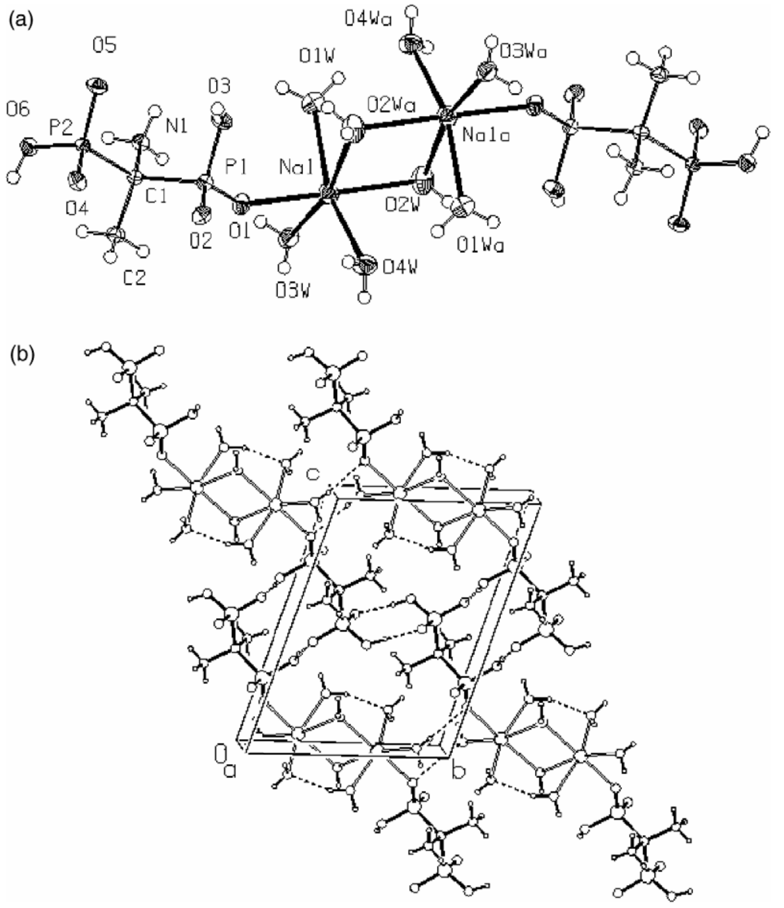

Figure 2. (a) The ORTEP of **2** with thermal ellipsoids at the 50% probability; (b) 2D hydrogen network of **2** viewed along the *bc* plane.

form an infinite chain through strong hydrogen bonds: O(6)–H(7) $\cdots$ O(4)#9 2.5593(14) Å (mode b). Two adjacent chains connect via two P–O–H $\cdots$ O–P hydrogen bonds (O(3)–H(8) $\cdots$ O(5)#3 2.6735(15) Å, mode a) and form a 12–member ring. Therefore, two-dimensional (2D) hydrogen bond networks are constructed by strong O–H $\cdots$ O bond interactions, shown in figure 2(b). In addition, N–H $\cdots$ O and Ow–H $\cdots$ O extend the 2D hydrogen network to 3D supramolecular structure.

3.3. *Crystal structure of 3*

As shown in figure 3(a), **3** crystallizes in monoclinic space group $P2(1)/c$. Similar to **1** and **2**, each $AEDPH_4$ loses one proton to NH_3 and transfers one to the nitrogen atom in the ligand for charge balance. The $AEDPH_3^-$ forms a 3D supramolecular structure by various hydrogen bonds including modes a, c and d as shown in figure 3(b). The strongest hydrogen bond is O(1)–H(4) $\cdots$ O(4)#6 2.5462(14) Å, which links the $AEDPH_3^-$ to form

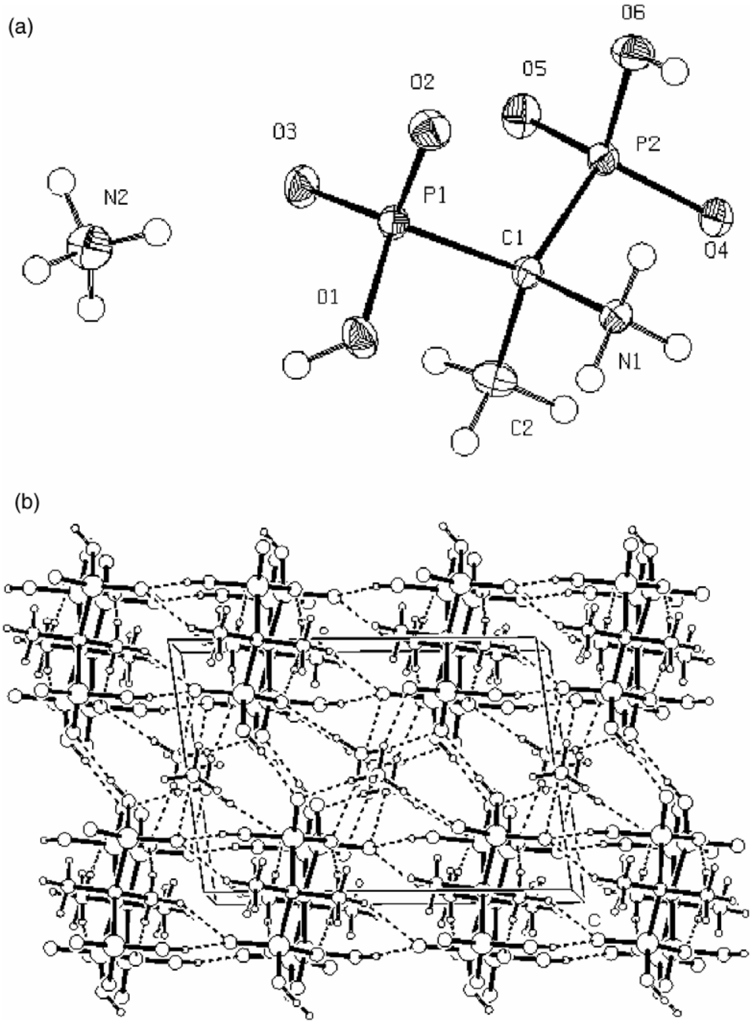

Figure 3. (a) ORTEP of **3** with thermal ellipsoids at the 50% probability; (b) 3D hydrogen network of **3** with encapsulating proton amino cation.

an infinite chain along the *a* axis. The O(6)–H(5) ··· O(2)#5 2.5886(15) Å and three N–H ··· O bonds (mode c) connect the one-dimensional (1D) chains to a 3D hydrogen bond system. The protonated amino cations lie in the channels of the hydrogen bond framework and link to the host via five N–H ··· O bonds: (N(2)–H(1N2) ··· O(5)#4 2.8047(16), N(2)–H(3N2) ··· O(3)#3 2.8259(17), N(2)–H(4N2) ··· O(2)#1 3.0393(16), N(2)–H(2N2) ··· O(4)#2 2.8181(16) and N(2)–H(4N2) ··· O(1) 3.0564(16) Å).

3.4. *Crystal structure of 4*

The ORTEP diagram of **4** is shown in figure 4(a), containing one $AEDPH_3^-$, one protonated $(CH_3)_2NH_2^+$ and one water molecule. In the synthesis, the DMF

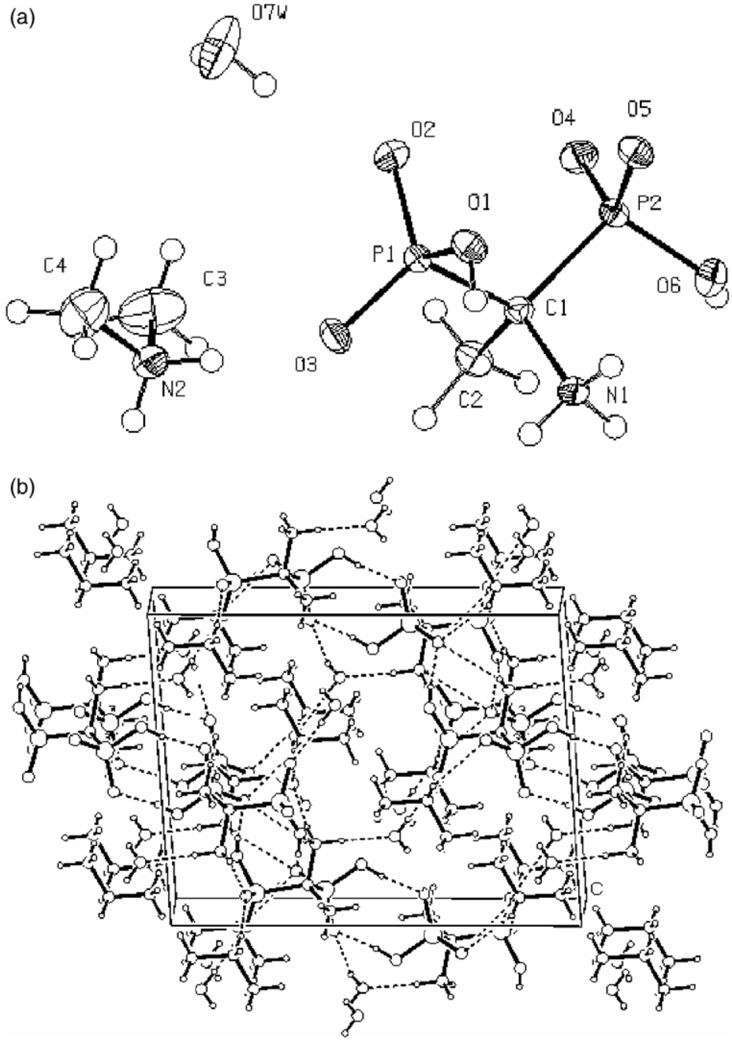

Figure 4. (a) The ORTEP of **4** with thermal ellipsoids at the 50% probability; (b) 2D hydrogen bond layers of **4**.

decomposes and changes to dimethylammonium. Different than **3**, the $AEDPH_3^-$ forms a dimer linked by a hydrogen bond O(6)–H(2) $\cdots$ O(4)#6 2.5589(13) Å (mode b). Furthermore, the dimeric anions connect three dimers by O–H $\cdots$ O (O(1)–H(1) $\cdots$ O(5)#5 2.5429(13) Å, mode a) and six N–H $\cdots$ O (mode c). As shown in figure 4(b), 2D hydrogen bond layers are constructed by these $AEDPH_3^-$, and the $(CH_3)_2NH_2^+$ cation and water molecule lie in the interlayer.

In the four compounds **1**–**4**, the $AEDPH_4$ deprotonates one proton and transfers one to the amino-N atom, serving as a -1 anion. The P–O, P–C bond lengths vary in the ranges 1.4863(12)–1.5809(10) and 1.8381(16)–1.8524(12) Å, in agreement with corresponding values [10, 12]. The different coordination modes of the cations are responsible for the structural difference of the four compounds.

Compared with other monovalent diphosphonates, lithium ion is always tetrahedrally coordinated by four oxygen atoms, while Na^+ has various coordination modes, similar to that in disulfonates [26]. $Na_2[(HO_3PCH_2)_3NH]\cdot 1.5H_2O$ [9] consists of two types of NaO_6 octahedra forming tetramers Na_4O_{16}. $Na(HO_3PC_6H_5)(H_2O_3PC_6H_5)$, $[Na\{HO_3P(CH_2)_2PO_3H_2\}]$ [10, 12], $Na_2[(HO_3PCH_2)NC_4H_8N(CH_2PO_3H)](H_2O)_8\cdot 2H_2O$ [11] and compound **2** have an edge-shared Na_2O_{10} unit, with the Na_2O_{10} in the two latter compounds bridged by two water molecules. Different to alkali metal phosphonates, the phosphonates of ammonium are all proton-transfer salts.

For monovalent diphosphonates, the structures vary from zero-, one-, two- to three-dimensional networks based on the different diphosphonic acids. The results illustrate the structural diversity with different metal ions and ligands, and the molar ratios of them. New functional inorganic-organic hybrids may be designed and synthesized as candidates for advanced material by rational selection of suitable ligands and metal ions.

4. IR and TG

Infrared spectra (IR) of compounds **1**–**4** are shown in figure 5(a). Compounds **1**, **2** and **4** have vibrations centered at 3500 cm^{-1}, showing the existence of water, confirmed by structure analysis. The stretching and bending vibration of NH_3^+ are 3200 cm^{-1} and 1400 cm^{-1}. The P–O stretching vibrations in the region 1150–900 cm^{-1}, the O–P–O bending vibrations in the region 540–410 cm^{-1} are common features [27].

Thermal gravimetric analysis (TG) for compounds **1**–**4** are depicited in figure 5(b). The curves show compound 1 is stable under 180°C in air. From 180 to 240°C, **1** has a rapid weight loss corresponding to dehydration; the dehydration weight loss is about 8.00% (Calcd 7.88%). The dehydration product of **1** shows a different X-Ray diffraction pattern from **1**, suggesting the change in structure after removal of water. The $Li(AEDPH_3)$ starts to decompose at 240°C, the residue at 900°C is probably LiP_{2O5} (65.90%, Calcd 65.02%). Different to compound **1**, the dehydration temperature of **2** is 90°C, lower than that of **1**, **3** and **4**. Compound **3** is stable until 250°C, and then decomposes rapidly. The last residule is uncharacterized. Compound **4** is stable under 170°C, and then rapidly loses dimethylammonium and water of the crystal lattice. The final TG curve is similar to **1** and **2**.

5. Conclusion

Four new monovalent 1-aminoethylidenephosphonates have been synthesized and characterized by EA, TG, IR and single crystal analysis. The lithium compound is a 24-metallacrown-6 lithium structure; sodium compound is binuclear bridged by water molecules. Compounds of amino and dimethylammonium are proton-transfer salts. The differences of the four aminophosphonates is related to the monovalent ions,

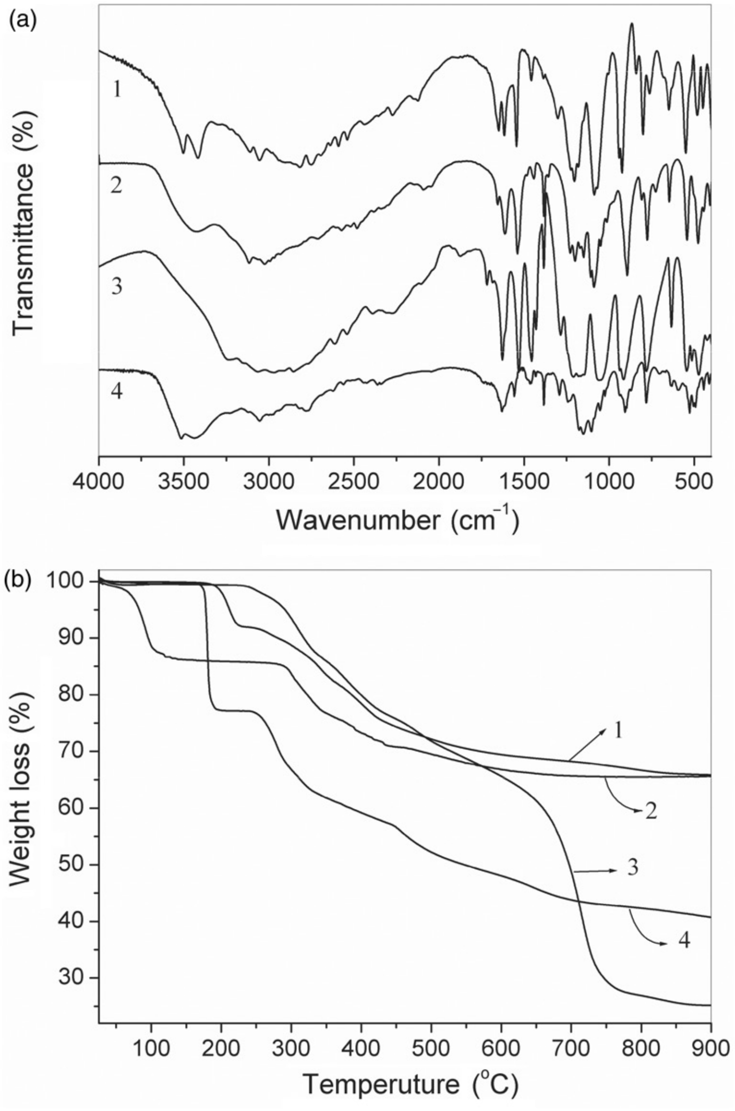

Figure 5. The IR spectra (a) and TG (b) for compounds **1**–**4**.

but are extended to 2D or 3D supramolecules by predictable hydrogen bonds of $AEDPH_3^-$.

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Supplementary material

Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Centre as Supplementary Publication. No. CCDC 287018(1), 299390(2), 299391(3) and 299394(4). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12, Union Road, Cambridge CB21EZ, UK (Fax: (+44) (1223) 336033; Email for inquiry: deposit@ccdc.cam.ac.uk).

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