The crystal structure of the anionic zinc-[amino(iminio)methyl]phosphonate one-dimensional coordination polymer, Zn-AIMP, is reported; the negative charge is balanced by an oxidanium cation (H₃O⁺) to give the composition [{(H₃O)[Zn(CH₄N₂PO₃)₃]}]ₙ. The building unit of the coordination polymer comprises a divalent Zn²⁺ cation (site symmetry 3_) and three [amino-(iminio)methyl]phosphonate mono-anionic ligands (point group symmetry m). The AIMP ligand exists in a zwitterionic form with a total charge −1 as the phosphonate is fully deprotonated (−PO₃²⁻), while the amino(iminio)methyl moiety is protonated (H₂N—C—NH₂⁺).

Structure description

The chemistry of phosphonic acids was initiated by the need for hydrolysis-resistant replacements for polyphosphates. Synthetic access to a variety of phosphonic acid structures is possible through several well-established routes (Sevrain et al., 2017). To the inorganic chemist, phosphonic acids are a valuable synthetic tool as versatile ligands for generating a plethora of metal phosphonate compounds that present diverse structural architectures, from molecular complexes, to chains and layers, to framework structures (Clearfield & Demadis, 2012). Herein, we report a new Zn²⁺ phosphonate one-dimensional anionic coordination polymer that contains the ligand [amino(iminio)methyl]phosphonate ([{Zn(CH₄N₂PO₃)₃]}⁻]ₙ, Zn-AIMP) and an oxidanium (H₃O⁺) cation. The ligand AIMP was generated in situ during the synthesis by the decomposition of the hexaethyl 1,3,5-triazine-2,4,6-triyltris(phosphonate) ester upon dealkylation with trimethylbromosilane.

The crystal structure of amino(iminio)methyl]phosphonate (obtained by decomposition of the ester hexaethyl 1,3,5-triazine-2,4,6-triyltris(phosphonate) via acid hydrolysis...
and subsequent heating at 373 K) has been reported in the literature (Yang et al., 2010). Interestingly, the sulfonate analogue of AIMP, aminoiminomethanesulfonic acid (NH₂)₂CSO₃ has been reported, and its crystal structure shows that this is also a zwitterion (Makarov et al., 1999). Our de-alkylation approach of the hexaethyl 1,3,5-triazine-2,4,6-triytriis(phosphonate) ester to yield the acid under mild conditions and with the use of trimethylbromosilane did not lead to the desired (1,3,5-triazine-2,4,6-triytriis(phosphonic acid) product, but to AIMP.

AIMP exists as a zwitterion in acidic solutions and it is neutral. However, at the pH of the reaction with Zn²⁺, its second phosphonic acid group is deprotonated, thus generating the AIMP anion. The Zn:AIMP molar ratio in Zn-AIMP is 1:3. Upon careful examination, the +2 charge of Zn²⁺ is offset by three mono-anionic AIMP ligands, offering a total charge of −3. In the absence of any other cations in solution, the excess −1 charge per building unit is balanced by an oxidanium cation that is generated by protonation of water (from the solvent). Zn-AIMP is a one-dimensional coordination polymer, its chains extending parallel to the c axis. The Zn²⁺ cation has a slightly distorted octahedral geometry, as illustrated in Fig. 1, coordinated exclusively by six phosphonate oxygen atoms from six different AIMP ligands. The Zn—O distance is 2.0927 (16) Å, which falls in the expected Zn—O(phosphonate) range (Colodrero et al., 2010). Each AIMP ligand bridges two neighbouring Zn²⁺ cations, Fig. 1.

The phosphonate group in the AIMP ligand is fully deprotonated, while the N—C—N moiety is protonated, hence each N atom bears two H atoms. From symmetry, the C₁—N₁ bonds are equivalent, with the bond length at 1.310 (3) Å being intermediate between those of a single and a double bond. The C—N bond length is comparable to that found in ‘free’ AIMP [1.299 (5) Å and 1.314 (5) Å; Yang et al., 2010].

The P—O bond lengths are 1.4957 (15) Å (coordinating) and 1.527 (2) Å (non-coordinating). It is reasonable to assume that the −2 charge on the phosphonate group is delocalized over all three O atoms. However, the P₁—O₂ bond (non-coordinating) is substantially longer than the P₁—O₁ bond (coordinating) and this can be rationalized by the formation of hydrogen bonds between O₂ with two two N—H moieties and the oxidanium cation (see below). The packing of the chains in Zn-AIMP along the b- and c-axis directions is shown in Fig. 2 (left and middle). The linear chains (intra-chain Zn—Zn—Zn angle = 180°) are packed parallel to the c axis. The oxidanium cation sits close to the non-coordinating P—O moiety of the chain and close to the N—C—N moiety of the neighbouring chain. The arrangement of the oxidanium cations (viewed down the c axis) is better described as staggered triangles that are ~4.75 Å apart, see Fig. 2 (right).
The presence of several hydrogen-bond donors and acceptors in the structure creates hydrogen-bonding schemes that deserve some discussion, see Fig. 3. First, the H$_2$O$^+$ cation is located between the chains and utilizes all its H atoms to form three strong hydrogen bonds with three different non-coordinating phosphonate O atoms originating from three neighbouring chains [O···O distance = 2.520 (3) Å, O3—H3···O2 angle = 155°, see Table 1 for symmetry codes]. Presumably, the H$_2$O$^+$ cations fill the intra-chain void space and stabilize the packing of the one-dimensional chains. It is noted the oxidanium-O3 atom, which is statistically disordered (see Refinement), does not form a close interaction along the threefold axis it resides upon of less than 3.6 Å. In addition, the chains further interact via hydrogen bonds that include the cationic [H$_2$N—C—NH$_2$]$^+$ moiety with phosphonate O atoms.

Synthesis and crystallization

Reagents and materials All starting materials were obtained from commercial sources and used without further purification. Ion-exchange column-deionized (DI) water was used for all syntheses. The starting reagents triethyl phosphite (98%), cyanuric chloride (98%) and zinc nitrate hexahydrate were from Alfa Aesar. The solvents petroleum ether, acetonitrile, cyanuric chloride (98%) and zinc nitrate hexahydrate were all syntheses. The starting reagents triethyl phosphite (98%), cyanuric chloride (98%) and zinc nitrate hexahydrate were from commercial sources and used without further purification.

Syntheses of [amino(iminio)methyl]phosphonate (AIMP). AIMP was synthesized from the dealkylation of the hexaethyloxy ester of 1,3,5-triazine-2,4,6-triytris(phosphonate). The latter was synthesized based on the synthetic procedure reported in the literature (Morrison, 1957) with modifications (Maxim et al., 2010). Yield: 0.916 g, 92%. The ‘as synthesized’ solid ester (pure by NMR) was then dealkylated using trimethylbromosilane, as follows. In a dry vial the ester (0.490 g, 1.0 mmol) and trimethylbromosilane (1044 µL, 8.0 mmol) were dissolved in acetonitrile (10 ml). The solution was stirred for 24 h, and the colour changed from faint orange to dark orange. Then the homogenous orange solution was left to stand at ambient temperature to allow evaporation of the solvent, yielding an orange oil. Methanol (10 ml) was added to remove the trimethylsilyl group from the phosphonate moiety (as its methoxy ester), and the mixture was stirred for 1 h to allow precipitation of the desired AIMP product (Yield: 0.598 g, 60%). $^{13}$C NMR (75.5 MHz, DMSO-d$_6$) $\delta$ 169.71 (d). $^{31}$P NMR (121.5 MHz, DMSO-d$_6$) $\delta$ 2.85.

Synthesis of [(H$_2$O)[Zn(CH$_3$N$_2$PO$_3$)$_3$]]$_n$ (Zn-AIMP). The synthesis of Zn-AIMP was performed at ambient temperature. Specifically, AIMP (0.016 g, 0.071 mmol) an excess was used, as it was found to give a product with better crystallinity) was dissolved in DI water (7 ml), Zn(NO$_3$)$_2$·6H$_2$O (0.005 g, 0.017 mmol, dissolved in 1 ml DI water) was added, and the pH was adjusted to ~3.5 using nitric acid. After 30 days a crystalline precipitate appeared, which was isolated by filtration and rinsed with a small amount of water (Yield: 0.001 g, 13%). The crystal used for measurement was handled under inert conditions, being manipulated while immersed in a perfluoropolyether protecting oil, and was mounted on a MiTeGen Micromount®.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The oxygen atom of the H$_2$O$^+$ present discussed.
cation falls on a threefold axis and is disordered with respect to a mirror plane over two half-occupied O-atom positions. No further constraints were necessary to model the disorder.

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full crystallographic data

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*catena-Poly[oxidanium [tris[µ-[amino(iminio)methyl]phosphonato]zincate(II)]]*

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*catena-Poly[oxidanium [tris[µ-[amino(iminio)methyl]phosphonato]zincate(II)]]*

Crystal data

(H$_3$O)$_2$[Zn(CH$_4$N$_2$PO)$_3$]  
$D_r = 2.023$ Mg m$^{-3}$  
Ag Kα radiation, $λ = 0.56086$ Å  
Cell parameters from 1652 reflections  
$θ = 3.4–21.3°$  
$μ = 1.06$ mm$^{-1}$  
$T = 298$ K  
Prism, colourless  
$0.12 × 0.11 × 0.09$ mm

Data collection

Bruker D8 Venture diffractometer  
6814 measured reflections  
608 independent reflections  
534 reflections with $I > 2σ(I)$  
$R_{int} = 0.062$  
$θ_{max} = 21.3°$, $θ_{min} = 2.6°$  
$h = −12→12$  
$k = −12→10$  
$l = −12→12$

Refinement

Refinement on $F^2$  
Hydrogen site location: mixed  
Least-squares matrix: full  
H atoms treated by a mixture of independent and constrained refinement  
$R[F^2 > 2σ(F^2)] = 0.027$  
$wR(F^2) = 0.072$  
$S = 1.13$  
$608$ reflections  
$43$ parameters  
$1$ restraint  
$Δρ_{max} = 0.28$ e Å$^{-3}$  
$Δρ_{min} = −0.50$ e Å$^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. All hydrogen atoms were located in difference Fourier maps and included as fixed contributions riding on attached atoms with isotropic thermal displacement parameters 1.2 or 1.5 times those of the respective carrier atom.
### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

|     | x           | y           | z           | \(U_{\text{iso}}/U_{\text{eq}}\) | Occ. (<1) |
|-----|-------------|-------------|-------------|----------------------------------|-----------|
| Zn1 | 0.000000    | 0.000000    | −0.500000   | 0.01420 (19)                     |           |
| P1  | −0.00820 (9)| 0.24927 (9) | −0.750000   | 0.0108 (2)                       |           |
| O2  | −0.0548 (3) | 0.3813 (3)  | −0.750000   | 0.0223 (5)                       |           |
| O1  | −0.05380 (19)| 0.1544 (2) | −0.61573 (16)| 0.0187 (4)                       |           |
| N1  | 0.2927 (3)  | 0.4198 (3)  | −0.6296 (2) | 0.0256 (5)                       |           |
| H1A | 0.395890    | 0.485001    | −0.628272   | 0.031*                           |           |
| H1B | 0.239885    | 0.386350    | −0.551784   | 0.031*                           |           |
| C1  | 0.2161 (4)  | 0.3713 (4)  | −0.750000   | 0.0148 (6)                       |           |
| O3  | −0.333333   | 0.333333    | −0.8104 (8) | 0.0351 (16)                      | 0.5       |
| H3  | −0.238480   | 0.340450    | −0.762355   | 0.15 (4)*                        | 0.5       |

### Atomic displacement parameters (Å²)

|     | \(U^{11}\) | \(U^{22}\) | \(U^{33}\) | \(U^{12}\) | \(U^{13}\) | \(U^{23}\) |
|-----|------------|------------|------------|------------|------------|------------|
| Zn1 | 0.0155 (2) | 0.0155 (2) | 0.0115 (3) | 0.00776 (12)| 0.000      | 0.000      |
| P1  | 0.0106 (4) | 0.0102 (4) | 0.0112 (4) | 0.0049 (3) | 0.000      | 0.000      |
| O2  | 0.0176 (12)| 0.0148 (12)| 0.0367 (14)| 0.0096 (10)| 0.000      | 0.000      |
| O1  | 0.0184 (8) | 0.0226 (9) | 0.0144 (8) | 0.0099 (7) | 0.0019 (6) | 0.0064 (6) |
| N1  | 0.0158 (10)| 0.0259 (11)| 0.0232 (11)| 0.0015 (9) | −0.0035 (8)| 0.0017 (8) |
| C1  | 0.0121 (14)| 0.0104 (14)| 0.0220 (15)| 0.0057 (12)| 0.000      | 0.000      |
| O3  | 0.0222 (19)| 0.0222 (19)| 0.061 (4)  | 0.0111 (10)| 0.000      | 0.000      |

### Geometric parameters (Å, °)

| Bond/Atom | Distance/Angle |
|-----------|----------------|
| Zn1—O1i   | 2.0927 (16)    |
| Zn1—O1ii  | 2.0927 (16)    |
| Zn1—O1iii | 2.0927 (16)    |
| Zn1—O1    | 85.04 (6)      |
| Zn1—O1iv  | 94.96 (6)      |
| Zn1—O1v   | 180.0          |
| Zn1—O1vi  | 149.57 (15)    |
| Zn1—O1vii | 112.38 (8)     |
| Zn1—O1    | 94.96 (6)      |
| Zn1—O1v   | 112.38 (8)     |
| Zn1—O1iv  | 116.94 (14)    |
| Zn1—O1v   | 105.92 (8)     |
| Zn1—O1v   | 105.92 (8)     |
| Zn1—O1    | 140.57 (15)    |
| Zn1—O1v   | 120.0          |
| Zn1—O1v   | 120.0          |
| Zn1—O1    | 119.02 (15)    |
| Zn1—O1v   | 119.02 (15)    |

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data-2
O1ii—Zn1—O1iii 180.0  N1—Cl—N1vi 121.6 (3)
O1ii—Zn1—O1i  94.96 (6)  O3vi—O3—H3 62.3
O1i—Zn1—O1i  85.04 (6)

O2—P1—O1—Zn1  −161.51 (15)  O1—P1—Cl—N1i  155.6 (2)
O2—P1—C1—N1  86.8 (2)  O1vi—P1—Cl—N1vi  30.8 (3)
O2—P1—C1—N1vi  −86.8 (2)  O1vi—P1—Cl—N1  −30.8 (3)
O1vi—P1—O1—Zn1  66.3 (2)  Cl—P1—O1—Zn1  −51.35 (19)
O1vi—P1—C1—N1  −155.6 (2)

Symmetry codes: (i) y, −x+y, −z−1; (ii) −x+y, −x, z; (iii) −x, −y, −z−1; (iv) −y, x−y, z; (v) x−y, x, −z−1; (vi) y, −x−y, −x, −z−3/2; (vii) −y+x−1, −x, −z−3/2.

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|---------|
| N1—H1A···O2viii | 0.86 | 2.19  | 2.925 (3) | 143     |
| N1—H1B···O1i  | 0.86 | 2.16  | 2.926 (3) | 147     |
| O3—H3···O2    | 0.98 | 1.59  | 2.520 (3) | 155     |

Symmetry codes: (i) y, −x+y, −z−1; (viii) y+1, x−y+1, z.