Crystal structure of (1-hydroxy-1-phosphono-pentyl)-phosphonic acid dimethyl ammonium salt, C7H21NO7P2, and of (1,8-dihydroxy-1,8,8-tris-phosphono-octyl)-phosphonic acid bis-dimethylammonium salt tetra-hydrate, C12H36N2O14P4 · 4H2O, evidence for trapped alcalkine species by bisphosphonic and tetraphosphonic acids in the crystalline state

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Abstract
C7H21NO7P2, triclinic, P1̅ (No. 2), a = 11.404(2) Å, b = 10.426(2) Å, c = 6.199(2) Å, α = 92.1(1)°, β = 95.9(1)°, γ = 110.5(1)°, V = 684.9 Å³, Z = 2, R_p(F) = 0.061, wRifd(F²) = 0.160, T = 291 K.

C12H36N2O14P4, triclinic, P1 (No. 2), a = 10.052(2) Å, b = 9.336(2) Å, c = 8.289(2) Å, α = 98.4(1)°, β = 104.9(1)°, γ = 106.6(1)°, V = 699.9 Å³, Z = 1, R_p(F) = 0.084, wRifd(F²) = 0.209, T = 291 K.

Source of material
The syntheses of the acids C5H14O7P2 and C8H22O14P4 have already been reported [1,2]. Crystallizations were done by slow evaporation from methanolic solutions at room temperature: 0.1 g of C5H14O7P2 or C8H22O14P4 were dissolved in 25 ml of methanol:water (1:1). By slow evaporation, only oily products were obtained. If a separate solution of dimethylamine is set in the vicinity of the crystallization pot, the dimethylamonium salts (C7H21NO7P2, C12H36N2O14P4 · 4H2O) shortly crystallize as large prisms.

Experimental details
All H atoms were initially calculated at idealized positions and refined with C-H and O-H distances restraints. An isotropic displacement parameter was set for each hydrogen in HBPA and BHTP, riding 1.2 times of the value for the bonded atom.

Discussion
The hydroxy-bisphosphonic acid HBPA and the bishydroxy-tetraphosphonic acid BHTP are very efficient compounds for complexing metallic ions and for their transport properties in biological media [3-5]. The wide application of HBPA and BHTP ranges from their use in bone scintigraphy [6] to the extraction of trans actinides in nuclear industry [7]. In addition, several amino substituted hydroxy-bis phosphonic acids are under evaluation in medicinal treatment of bone deseases as they strongly interact and regulate the transport of calcium [3,8]. Most of these biological active bis-acids have an extended alkyl-amino chain linked to the central carbon. In this respect, the crystal structures of these uncomplexed amino phosphonic acids are zwitterionic species like amino-acids. HBPA and BHTP without amino function at C(1) show superacid properties [9,10]. These compounds as free acids have poor crystalline properties although a number of structures have been reported [10-13]. In this communication, it is given evidence that they can trap and stabilize cationic species derived from volatile alcalkine compounds like dimethylamine to give particularly stable crystals. A possible catalytic intermolecular dehydration of methanol, the solvent used in crystallizations, cannot be ruled out because of the superacid properties of the title compounds. This will lead to a dimethyloxonium cation [14] with a similar density signature than dimethylammonium. To confirm the nature of the central atom of the cation (N or O) and for accurate hydrogen bond location, a neutron study on HBPA has been undertaken. This study will be published elsewhere [15].

1. (1-Hydroxy-1-phosphono-pentyl)-phosphonic acid dimethyl ammonium salt, C7H21NO7P2

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### Table 1. Data collection and handling.

| Crystal: | colourless, irregular, size 0.2 x 0.2 x 0.3 mm |
|----------|-----------------------------------------------|
| Wavelength: | Cu Kα radiation (1.54180 Å) |
| μ: | 31.26 cm⁻¹ |
| Diffractometer, scan mode: | Philips PW1100, θ/2θ |
| 2θmax: | 128.04° |
| N(hkl)measured, N(hkl)unique: | 1790, 1790 |
| Criterion for Iobs, I(hkl)g: | Iobs > 2σ(Iobs), 1776 |
| N(param)refined: | 163 |
| Programs: | SHELXS-86 [16], SHELXL-97 [17], Xtal-GX [18] |

### Table 2. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x | y | z | U11 | U22 | U33 | U12 | U13 | U23 |
|------|------|---|---|---|-----|-----|-----|-----|-----|-----|
| P(1) | 2i  | 0.38297(8) | 0.0808(1) | 0.1529(1) | 0.0287(5) | 0.0162(7) | 0.0107(5) | 0.0147(4) | -0.0020(4) | 0.0059(4) |
| P(2) | 2i  | 0.35859(8) | -0.3216(1) | -0.0715(1) | 0.0285(5) | 0.0121(7) | 0.0195(5) | 0.0124(4) | -0.0006(4) | 0.0057(5) |
| O(12) | 2i  | 0.3869(2) | -0.0661(3) | 0.0891(4) | 0.029(1) | 0.014(2) | 0.033(2) | 0.011(1) | 0.001(1) | 0.009(1) |
| O(11) | 2i  | 0.5106(3) | 0.0840(3) | 0.2379(4) | 0.032(1) | 0.020(2) | 0.019(1) | 0.017(1) | -0.004(1) | 0.004(1) |
| O(13) | 2i  | 0.3230(3) | 0.1495(3) | 0.3151(4) | 0.047(2) | 0.036(2) | 0.015(1) | 0.030(2) | 0.004(1) | 0.006(1) |
| O(21) | 2i  | 0.6384(2) | 0.2673(3) | -0.1274(4) | 0.031(1) | 0.018(2) | 0.031(1) | 0.017(1) | 0.006(1) | 0.010(1) |
| O(22) | 2i  | 0.5616(2) | 0.3980(3) | 0.149(4) | 0.042(2) | 0.018(2) | 0.019(1) | 0.020(1) | -0.007(1) | -0.000(1) |
| O(23) | 2i  | 0.5233(3) | 0.4147(3) | -0.2589(4) | 0.043(2) | 0.019(2) | 0.019(1) | 0.021(1) | 0.004(1) | 0.012(1) |
| O(1) | 2i  | 0.3740(2) | 0.0915(3) | -0.2838(4) | 0.038(1) | 0.018(2) | 0.009(1) | 0.020(1) | -0.005(1) | -0.002(1) |
| C(11) | 2i  | 0.3851(3) | 0.1787(4) | -0.0912(5) | 0.031(2) | 0.021(2) | 0.011(2) | 0.016(2) | 0.000(1) | 0.009(2) |
| C(2) | 2i  | 0.2759(3) | 0.2313(4) | -0.1215(6) | 0.030(2) | 0.018(2) | 0.019(2) | 0.014(2) | -0.001(1) | 0.006(2) |
| C(3) | 2i  | 0.1444(4) | 0.1219(5) | -0.1484(7) | 0.030(2) | 0.026(3) | 0.039(2) | 0.013(2) | -0.002(2) | 0.011(2) |
| C(4) | 2i  | 0.0409(4) | 0.1779(5) | -0.2161(8) | 0.029(2) | 0.040(3) | 0.046(3) | 0.016(2) | -0.002(2) | 0.013(2) |
| C(5) | 2i  | 0.0298(5) | 0.2804(7) | -0.049(1) | 0.051(3) | 0.083(5) | 0.072(4) | 0.043(3) | 0.005(3) | 0.000(4) |
| N(1) | 2i  | 0.7185(3) | 0.3460(4) | 0.4759(5) | 0.030(2) | 0.033(2) | 0.021(2) | 0.011(2) | -0.003(1) | 0.006(2) |
| C(15) | 2i  | 0.7954(4) | 0.2680(6) | 0.4038(9) | 0.037(2) | 0.062(4) | 0.059(3) | 0.023(3) | -0.008(2) | -0.011(3) |
| C(25) | 2i  | 0.7898(5) | 0.4918(5) | 0.527(1) | 0.060(3) | 0.033(3) | 0.061(3) | 0.000(3) | 0.008(3) | 0.010(3) |

### Table 4. Data collection and handling.

| Crystal: | colourless, irregular, size 0.15 x 0.30 x 0.60 mm |
| Wavelength: | Cu Kα radiation (1.54180 Å) |
| μ: | 32.07 cm⁻¹ |
| Diffractometer, scan mode: | Philips PW1100, θ/2θ |
| 2θmax: | 123.92° |
| N(hkl)measured, N(hkl)unique: | 1538, 1538 |
| Criterion for Iobs, I(hkl)g: | Iobs > 2σ(Iobs), 1520 |
| N(param)refined: | 182 |
| Programs: | SHELXS-86 [16], SHELXL-97 [17], Xtal-GX [18] |
Table 5. Atomic coordinates and displacement parameters (in Å²).

| Atom | Site | x      | y      | z      | U₁₁  | U₂₂  | U₃₃  |
|------|------|--------|--------|--------|------|------|------|
| H(12)| 2i   | 0.2980 | 0.3702 | 0.2125 | 0.032|      |      |
| H(21)| 2i   | 0.1214 | 0.4979 | 0.7642 | 0.043|      |      |
| H(22)| 2i   | -0.0936| 0.3604 | 0.5749 | 0.037|      |      |
| H(1) | 2i   | 0.0664 | 0.0737 | 0.3438 | 0.027|      |      |
| H(21C)| 2i  | 0.3932 | 0.2914 | 0.6527 | 0.038|      |      |
| H(22C)| 2i | 0.2733 | 0.1443 | 0.6587 | 0.038|      |      |
| H(1C3)| 2i | 0.2737 | 0.0153 | 0.3953 | 0.038|      |      |
| H(2C3)| 2i | 0.3903 | 0.1630 | 0.3848 | 0.038|      |      |
| H(1C4)| 2i | 0.5610 | 0.1420 | 0.6143 | 0.044|      |      |
| H(2C4)| 2i | 0.4450 | 0.0006 | 0.6362 | 0.044|      |      |
| H(1NS)| 2i  | 0.8657 | 0.3642 | 0.1982 | 0.036|      |      |

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