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Key indicators

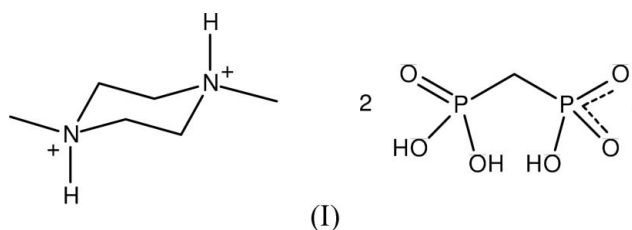
Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.028
 wR factor = 0.075
Data-to-parameter ratio = 15.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.***N,N'*-Dimethylpiperazinium(2+)
bis[methylenehydrogendiphosphonate(1-)]**

The asymmetric unit of the title compound, $\text{C}_6\text{H}_{16}\text{N}_2^{2+} \cdot 2(\text{HO})_2(\text{O})\text{PCH}_2\text{P}(\text{O})_2(\text{OH})^-$, contains two singly charged diphosphonate anions and two half-cations, each doubly charged cation lying on an inversion centre. Single deprotonation of methylenediphosphonic acid to give a salt with an organic amine is unprecedented, double deprotonation being normal. All N—H and O—H groups act as hydrogen-bond donors in the crystal structure, with unprotonated O atoms as the acceptors, giving a three-dimensional network.

Received 1 July 2005
Accepted 15 July 2005
Online 20 July 2005

Comment

Phosphonic and diphosphonic acids are extremely versatile building blocks in supramolecular chemistry (Farrell *et al.*, 2001; Ferguson *et al.*, 1998; Glidewell *et al.*, 2000; Wheatley *et al.*, 2001). An important factor in the behaviour of such acids is the marked difference in acidity for stepwise deprotonation of the two hydroxyl functions in each $-\text{PO}(\text{OH})_2$ group. With organic amines, typically only one proton per phosphonate group is transferred from O to N. The resulting $-\text{P}(\text{O})_2(\text{OH})-$ group can thus act as a hydrogen-bond donor as well as an acceptor. The structure of methyldiphosphonic acid itself (DeLaMatter *et al.*, 1973) consists of a three-dimensional hydrogen-bonded network.



The title compound, (I), obtained unintentionally in one of a series of hydrothermal syntheses of aluminium diphosphonate complexes, is a 1:2 salt of diprotonated piperazine (generated by coupling of trimethylamine under the hydrothermal conditions) and the singly charged anion of methylenediphosphonic acid obtained by removal of only one proton; the second phosphonic acid group remains uncharged. Although there appears to be no previous report of such a reaction of trimethylamine to produce *N,N'*-dimethylpiperazine, this product can be obtained from trimethylamine oxide by deprotonation (Beugelmans *et al.*, 1985).

The asymmetric unit of (I) contains two anions and two half-cations, each cation lying on an inversion centre (Fig. 1). Both independent piperazine rings have the expected chair conformation, with the methyl substituents equatorial. All H

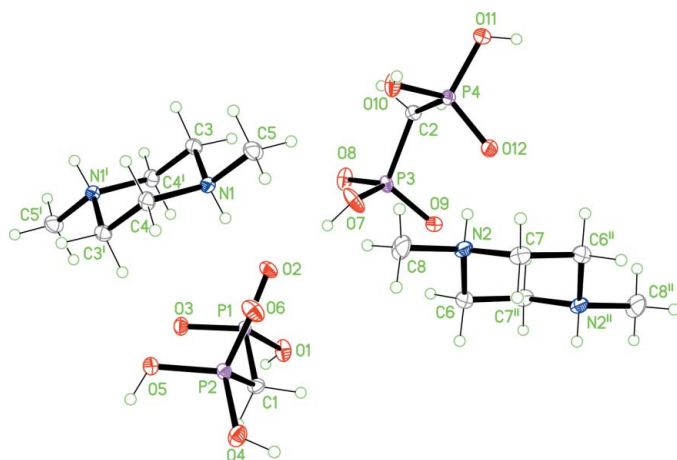


Figure 1

The two cations (completed by inversion symmetry) and two anions in the asymmetric unit of (I), showing atom labels and with 50% probability displacement ellipsoids. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.]

atoms bonded to N in the cations and to O in the anions were clearly identified in a difference map. The P—O bond lengths to the OH groups are all longer than those to unprotonated O atoms (Table 1). The shortest P—O bonds (P2—O6 and P4—O12) are found in the intact P(O)(OH)₂ phosphonic acid groups of the anions and can be assigned as P=O double bonds. The P—O bonds to unprotonated O atoms in the deprotonated P(O)₂(OH) phosphonate groups are intermediate in length; these are delocalized and intermediate between single and double bonds and can be assumed to carry the delocalised negative charge, while the P—OH bonds are single. Methylidiphosphonates in crystal structures are usually dianionic, with both groups deprotonated. Only in one previous report is a singly charged H₂O₃PCH₂PO₃H[−] anion found (Hmimid *et al.*, 1987); in this triethylammonium(I) compound, singly and doubly charged anions occupy the same position and are, therefore, disordered.

All N—H and O—H groups act as hydrogen-bond donors in the crystal structure of (I) (Fig. 2, Table 2). The acceptors are the unprotonated O atoms of the anions; since there are only six of these for the eight donors, two (atoms O2 and O8, which carry some shared negative charge in the delocalized phosphonate groups) are double acceptors. The hydrogen bonding generates a three-dimensional network.

Experimental

The title compound was obtained by hydrothermal synthesis, in an attempt to prepare an aluminium methylenediphosphonate complex. A mixture of Al₂(SO₄)₃·18H₂O (98%, Alfa Aesar), methylenediphosphonic acid (98%, Alfa Aesar), hydrofluoric acid (48 wt.% in water, Aldrich), trimethylamine (48% in water, Fluka) and ethanol was combined in the molar ratio 1.3:9.43:9.52:100. Vigorous stirring led to complete dissolution of all reagents. The solution was then placed in a 23 ml Teflon-lined stainless steel autoclave and heated at 473 K for 10 d. The title compound, (I), was collected by filtration, washed with deionized water and air-dried. It is not known whether aluminium-containing products were in the resulting solid or in the filtrate. The solid material was largely an unidentified powder mixture containing single crystals of the title compound.

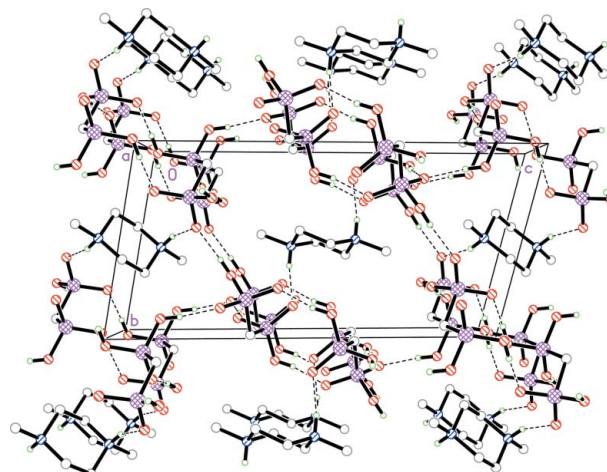


Figure 2

The packing of the ions, viewed down the *a* axis, with hydrogen bonds shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Crystal data

C₆H₁₆N₂²⁺·2CH₅O₆P₂[−]
M_r = 466.19
 Triclinic, *P* $\bar{1}$
a = 6.9881 (6) Å
b = 8.9148 (6) Å
c = 16.6251 (10) Å
 α = 98.910 (5)°
 β = 95.882 (6)°
 γ = 112.244 (6)°
V = 932.24 (12) Å³

Z = 2
D_x = 1.661 Mg m^{−3}
 Mo K α radiation
 Cell parameters from 59 reflections
 θ = 2.5–27.5°
 μ = 0.47 mm^{−1}
T = 120 (2) K
 Block, colourless
 0.50 × 0.50 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2002)
T_{min} = 0.800, *T_{max}* = 0.915
 12295 measured reflections

4037 independent reflections
 3592 reflections with *I* > 2 σ (*I*)
R_{int} = 0.028
 θ_{max} = 27.5°
h = −9 → 9
k = −11 → 11
l = −21 → 21

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.028
wR [*F*²] = 0.075
S = 1.06
 4037 reflections
 262 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0315P)^2 + 0.7406P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.55 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.50 \text{ e \AA}^{-3}$
 Extinction correction: SHELXTL (Sheldrick, 2001)
 Extinction coefficient: 0.011 (2)

Table 1

Selected bond lengths (Å).

P1—C1	1.8118 (16)	P3—C2	1.8088 (16)
P1—O1	1.5666 (12)	P3—O7	1.5646 (13)
P1—O2	1.5119 (11)	P3—O8	1.5312 (12)
P1—O3	1.5180 (11)	P3—O9	1.5055 (12)
P2—C1	1.8000 (16)	P4—C2	1.8021 (16)
P2—O4	1.5703 (12)	P4—O10	1.5494 (12)
P2—O5	1.5401 (11)	P4—O11	1.5583 (12)
P2—O6	1.4939 (12)	P4—O12	1.5005 (12)

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H1O···O6 ⁱⁱⁱ	0.81 (2)	1.73 (2)	2.5287 (16)	169 (2)
O4—H4O···O8 ^{iv}	0.83 (2)	1.76 (2)	2.5799 (17)	174 (2)
O5—H5O···O3 ^v	0.84 (2)	1.63 (2)	2.4689 (16)	177 (2)
O7—H7O···O2	0.83 (2)	1.71 (2)	2.5139 (16)	162 (2)
O10—H10O···O8 ^{vi}	0.82 (2)	1.73 (2)	2.5228 (17)	163 (2)
O11—H11O···O9 ^{vii}	0.83 (2)	1.70 (2)	2.5222 (17)	169 (2)
N1—H1N···O2	0.86 (2)	1.97 (2)	2.7802 (18)	157 (2)
N2—H2N···O12	0.88 (2)	1.79 (2)	2.6563 (18)	170 (2)

Symmetry codes: (iii) $x + 1, y, z$; (iv) $x - 1, y - 1, z$; (v) $-x + 1, -y, -z$; (vi) $x - 1, y, z$; (vii) $-x + 2, -y + 2, -z + 1$.

C-bound H atoms were positioned geometrically and refined with a riding model (including free rotation about C—C bonds), with C—H = 0.98 (CH₂) or 0.99 Å (CH₃) and with $U_{\text{iso}}(\text{H}) = 1.2$ (1.5 for methyl groups) times $U_{\text{eq}}(\text{C})$. H atoms bonded to N and O were located in a difference map and refined with restrained distances of N—H = 0.87 (2) Å and O—H = 0.84 (2) Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N}, \text{O})$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXTL*

(Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank the EPSRC, UK, for financial support.

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