Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

4,4′-Trimethylenedipyridinium bis[carboxymethylphosphonate(1−)]: a three-dimensional framework structure built from O—H···O, N—H···O and C—H···O hydrogen bonds

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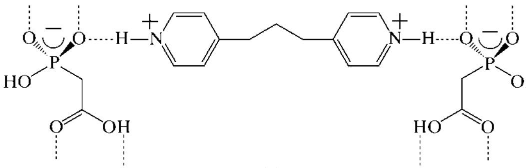
Received 27 May 2003
Accepted 28 May 2003
Online 22 July 2003

In the title compound, $C_{13}H_{16}N_2^{2+}\cdot 2C_2H_4O_5P^-$, the cation lies across a twofold rotation axis in space group *Fdd*2. The anions are linked into molecular ladders by two O—H···O hydrogen bonds [H···O = 1.73 and 1.77 Å, O···O = 2.538 (2) and 2.598 (3) Å, and O—H···O = 160 and 170°], these ladders are linked into sheets by a single type of N—H···O hydrogen bond [H···O = 1.75 Å, N···O = 2.624 (3) Å and N—H···O = 171°] and the sheets are linked into a three-dimensional framework by a single type of C—H···O hydrogen bond [H···O = 2.48 Å, C···O = 3.419 (4) Å and C—H···O = 167°].

Comment

We have described recently the supramolecular structures of the adducts formed by carboxymethylphosphonic acid [phosphonoacetic acid, $HOOCCH_2P(O)(OH)_2$] with both 4,4′-bipyridyl (NC_5H_4–C_5H_4N), where a 1:1 adduct is formed, and 1,2-bis(4-pyridyl)ethane (NC_5H_4–CH_2CH_2–C_5H_4N), where a 1:2 adduct is formed (Bowes *et al.*, 2003). These two adducts are both salts, with constitutions $C_{10}H_9N_2^+\cdot C_2H_4O_5P^-$ and $C_{12}H_{14}N_2^{2+}\cdot 2C_2H_4O_5P^-$, respectively. In the 4,4′-bipyridyl adduct, the anions form simple $C(4)$ chains that are linked by the cations into sheets of $R_6^6(38)$ rings, which in turn are linked by multiple C—H···O hydrogen bonds. In the 1,2-bis(4-pyridyl) adduct, on the other hand, the anions alone form sheets of alternating $R_2^2(12)$ and $R_6^6(28)$ rings, which are linked by the cations into a three-dimensional framework. Continuing this study, we have prepared and structurally characterized the title compound, (I), the adduct formed between 4,4′-trimethylenedipyridine and carboxymethylphosphonic acid.



(I)

Compound (I) (Fig. 1) is a salt, $[HNC_5H_4(CH_2)_3C_5H_4NH]^{2+}\cdot 2[HOOCCH_2P(O)_2(OH)]^-$, in which complete transfer of H atoms, to the N atom from one of the phosphonate O atoms, has occurred. The cation lies across a twofold rotation axis in space group *Fdd*2 and, for the reference cation, this axis was selected as that along ($\frac{1}{2}$, $\frac{1}{2}$, z). The anion lies in a general position. In the anion, the P—O and C—O distances (Table 1) are fully consistent with the H-atom locations deduced from difference maps. In the cation, the central C14—C17—C18—C17^i—C14^i fragment [symmetry code: (i) $1 - x$, $1 - y$, z] is effectively planar, with an all-*trans* conformation (Table 1), but the pyridinium ring is rotated out of this plane. All other bond lengths and angles have unexceptional values.

The ions are linked by a small number of hydrogen bonds (Table 2) into a single three-dimensional framework, in which it is possible to identify substructures in one and two dimen-

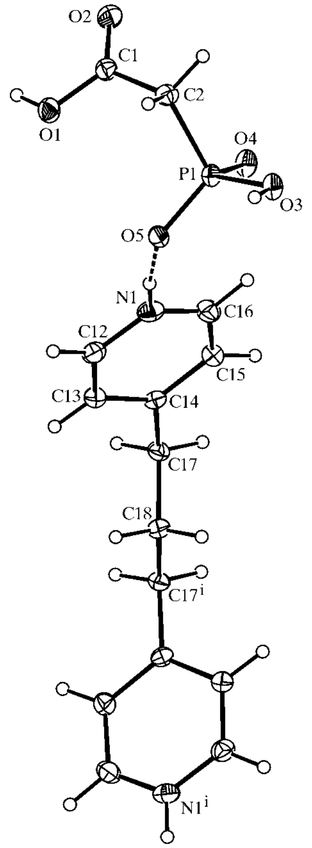


Figure 1
The independent components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x$, $1 - y$, z.]

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DOI: 10.1107/S0108270103011818

sions. The anions alone form a one-dimensional substructure in the form of a molecular ladder or a chain of edge-fused rings. The anions and cations are linked into sheets by a combination of all of the hard (Desiraju & Steiner, 1999) hydrogen bonds, all of which have $D\cdots A$ distances that are short for their type, and the sheets are themselves linked into a continuous framework by a single soft C—H$\cdots$O hydrogen bond.

Phosphonate atom O3 in the anion at (x, y, z) acts as a hydrogen-bond donor to phosphonate atom O4 in the anion at (x, y, $1 + z$), so generating by translation a $C(4)$ chain running parallel to the [001] direction. In addition, carboxy atom O1 at (x, y, z) acts as a hydrogen-bond donor to phosphonate atom O5 at ($1 - x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$), so producing a $C(6)$ chain parallel to [001] and generated by the 2_1 screw axis along ($\frac{1}{2}$, $\frac{1}{4}$, z). The combination of the $C(4)$ and $C(6)$ motifs generates a molecular ladder along [001] (Fig. 2), which can alternatively be regarded as a chain of edge-fused $R_3^3(16)$ rings. The anion substructure thus contains two of the three hydrogen-bonded motifs most characteristic of phosphonic acids and phosphonate anions, but the third such motif, namely $R_2^2(8)$ rings, is absent.

There are eight [001] ladders running through each unit cell, *viz*. two generated by each of the screw axes at $x = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$. For each of these values of x, the anion ladders are linked by cations, *via* N—H$\cdots$O hydrogen bonds, into (100) sheets. The N atoms at (x, y, z) and ($1 - x$, $1 - y$, z) are both components of the cation lying across the twofold rotation axis along ($\frac{1}{2}$, $\frac{1}{2}$, z). These atoms act as hydrogen-bond donors to phosphonate atoms O5 in the anions at (x, y, z) and ($1 - x$, $1 - y$, z), respectively, which lie in the anion ladders along ($\frac{1}{2}$, $\frac{1}{4}$, z) and ($\frac{1}{2}$, $\frac{3}{4}$, z), respectively. Propagation of these hydrogen bonds thus links all of the cations lying across rotation axes having $x = \frac{1}{2}$ and all of the anion ladders generated by 2_1 screw axes having $x = \frac{1}{2}$ into a (100) sheet built from $R_6^6(40)$ rings (Fig. 3).

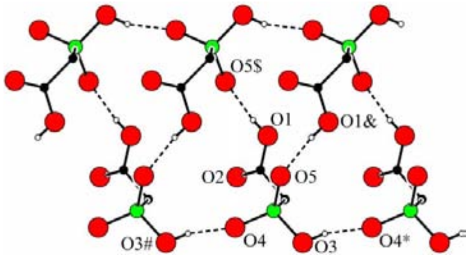

Figure 2
Part of the crystal structure of (I), showing the formation of a chain of edge-fused $R_3^3(16)$ rings containing anions only. For clarity, the unit-cell box and H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*), hash (#), dollar sign ($) or ampersand (&) are at the symmetry positions (x, y, $1 + z$), (x, y, $-1 + z$), ($1 - x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$) and ($1 - x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$), respectively.

Four (100) sheets pass through each unit cell, and these sheets are linked by C—H$\cdots$O hydrogen bonds (Table 2 and Fig. 4) into a three-dimensional framework. Atoms C13 at (x, y, z) and ($1 - x$, $1 - y$, z), which are components of the cation lying across the twofold rotation axis along ($\frac{1}{2}$, $\frac{1}{2}$, z), act as hydrogen-bond donors, respectively, to phosphonate atoms O4 in the anions at ($\frac{1}{4} + x$, $\frac{3}{4} - y$, $-\frac{1}{4} + z$) and ($\frac{3}{4} - x$, $\frac{1}{4} + y$, $-\frac{1}{4} + z$). These two anions lie, respectively, in the (100) sheets generated by the axes at $x = \frac{3}{4}$ and $\frac{1}{4}$, and propagation by the space group of this single type of soft hydrogen bond links all of the (100) sheets into a single framework.

Thus, a single type of hydrogen bond, namely O—H$\cdots$O, gives rise to a one-dimensional substructure; the combination of two types of hydrogen bond, namely O—H$\cdots$O and N—H$\cdots$O, gives rise to a two-dimensional substructure; and the combination of three types of hydrogen bond, namely O—H$\cdots$O, N—H$\cdots$O and C—H$\cdots$O, generates the entire three-dimensional structure. The anion substructure, in particular, differs from those found in the corresponding salts formed from 4,4′-bipyridyl and 1,2-bis(4-pyridyl)ethane.

In contrast to (I), the simple salt 4,4′-trimethylenedipyridinium dinitrate, (II) (Lee *et al.*, 2003), whose constitution precludes the formation of O—H$\cdots$O hydrogen bonds, contains just three-component aggregates containing a pair of N—H$\cdots$O hydrogen bonds, but with no significant C—H$\cdots$O hydrogen bonds between these aggregates. On the other hand, there are strong electrostatic interactions between adjacent

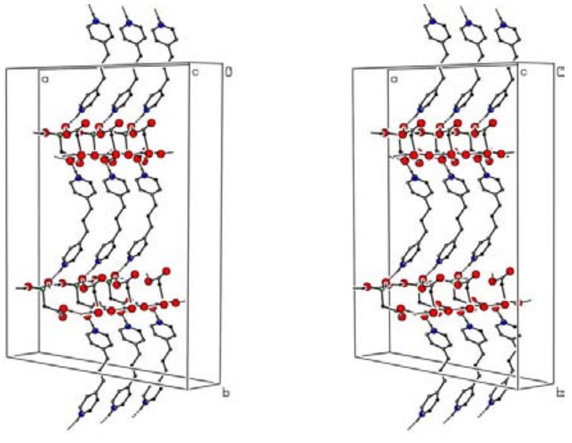

Figure 3
Stereoview of part of the crystal structure of (I), showing the formation, *via* the hard hydrogen bonds, of the (100) sheet at $x = \frac{1}{2}$.

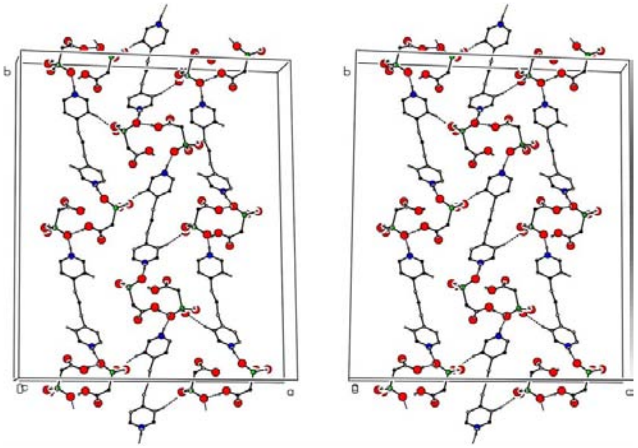

Figure 4
Stereoview of part of the crystal structure of (I), showing the linking of the (100) sheets into a single framework by a single type of C—H$\cdots$O hydrogen bond.

pyridinium rings and nitrate ions, whose planes are nearly parallel to one another. Note also the contrast between (II) and the hydrated nitrate, (III), formed by 1,2-bis(4-pyridyl)-ethane and containing a monoprotonated diamine (Almeida Paz *et al.*, 2003). In (III), the cations are linked into chains by N—H···N hydrogen bonds, and the nitrate ions and water molecules form hydrogen-bonded layers, but there are no hard hydrogen bonds between cations and anions.

Experimental

Stoichiometric quantities of 4,4′-trimethylenedipyridine and carboxymethylphosphonic acid (both purchased from Aldrich) were dissolved separately in methanol. The solutions were mixed and the mixture set aside to crystallize, providing analytically pure (I). Analysis found: C 42.8, H 5.2, N 5.8%; $C_{17}H_{24}N_2O_{10}P_2$ requires: zC 42.7, H 5.1, N 5.9%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$C_{13}H_{16}N_2^{2+}\cdot 2C_2H_4O_5P^-$
$M_r = 478.32$
Orthorhombic, *Fdd*2
$a = 27.366$ (2) Å
$b = 32.347$ (2) Å
$c = 4.8818$ (3) Å
$V = 4321.4$ (5) Å^3
$Z = 8$
$D_x = 1.470$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2418 reflections
$\theta = 2.9$–27.5°
$\mu = 0.26$ mm^{-1}
$T = 150$ (1) K
Needle, colourless
0.16 × 0.06 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.886$, $T_{\max} = 0.990$
7640 measured reflections
2418 independent reflections
1864 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$
$\theta_{\max} = 27.5°$
$h = -35 \rightarrow 34$
$k = -37 \rightarrow 42$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.103$
$S = 1.05$
2418 reflections
144 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 0.6064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00136 (19)
Absolute structure: Flack (1983), 1029 Friedel pairs
Flack parameter = 0.06 (13)

Crystals of (I) are orthorhombic and the space group *Fdd*2 was assigned uniquely from the systematic absences. All H atoms were located from difference maps and were subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic) or 0.99 Å (CH_2), N—H distances of 0.88 Å and O—H distances of 0.84 Å. The correct orientation of the structure with respect to the polar axis was established using the Flack (1983) parameter.

Table 1
Selected geometric parameters (Å, °).

P1—O3	1.568 (2)	C1—O1	1.317 (4)
P1—O4	1.495 (2)	C1—O2	1.214 (4)
P1—O5	1.511 (2)		
C13—C14—C17—C18	−65.0 (3)	C14—C17—C18—C17$^{\rm i}$	177.8 (2)

Symmetry code: (i) $1 - x, 1 - y, z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O5$^{\rm ii}$	0.84	1.77	2.598 (3)	170
O3—H3···O4$^{\rm iii}$	0.84	1.73	2.537 (3)	160
N1—H1*A*···O5	0.88	1.75	2.624 (3)	171
C13—H13···O4$^{\rm iv}$	0.95	2.48	3.419 (4)	167

Symmetry codes: (ii) $1 - x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $x, y, 1 + z$; (iv) $\frac{1}{4} + x, \frac{3}{4} - y, z - \frac{1}{4}$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a diffractometer purchased with funds from the NSERC, Canada.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1644). Services for accessing these data are described at the back of the journal.

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