Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Sodium methylenediphosphonate, $Na(HO_3PCH_2PO_3H_2)$

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Received 29 June 2005
Accepted 10 August 2005
Online 17 August 2005

The title compound, poly[sodium(I)-μ_6-methylenediphosphonato], $[Na(CH_5O_6P_2)]_n$, has been synthesized, and characterized by single-crystal diffraction methods and spectroscopic studies. It has a three-dimensional structure in which the Na^+ ions (site symmetry $\overline{1}$) are octahedrally coordinated by O atoms of the methylene diphosphonate moieties.

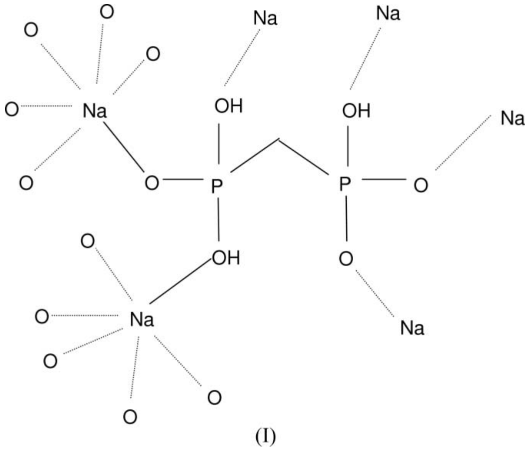
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(a–O) = 0.002 Å
R factor = 0.028
wR factor = 0.078
Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The solid-state chemistry of metal diphosphonates is an active area of research (Clearfield, 1998; Clearfield & Wang, 2002). Among the many alkyl diphosphonates known, there are only a few reports of compounds with a metal to diphosphonic acid ratio of 1:1. These include $Ti[O_3P(CH_2)_nPO_3]$ (n = 2 and 3; Serre & Ferey, 2001), $LnH[O_3P(CH_2)_nPO_3]$ (n = 1–3; Serpaggi & Ferey, 1998), $Sb[O_3P(CH_2)_nPO_3H]$ (n = 2 and 3; Adair *et al.*, 2000) and $Sn(HO_3PCH_2PO_3H)$ (Zapf *et al.*, 1996). As part of our ongoing studies of organic–inorganic hybrid materials, we have synthesized several alkyl diphosphonates of alkali metals, including the title compound, (I) (Fig. 1).



(I)

The title compound, $Na(HO_3PCH_2PO_3H_2)$, unlike the layered–pillared compound $Na(HO_3PCH_2CH_2PO_3H_2)$ (Rao, 2005), has a three-dimensional structure (Fig. 2). The two crystallographically distinct Na^+ ions occupy inversion centres and are octahedrally coordinated by O atoms of the diphosphonate moieties (Table 1). Atom Na1 is bonded, through atoms O1, O2 and O4, to two diphosphonate moieties in a bidentate fashion and to another two diphosphonate moieties in a monodentate fashion. Atom Na2 is bonded, through atoms O3, O5 and O6, to six diphosphonate moieties in a monodentate fashion (Fig. 2). The diphosphonate species is thus bonded to one Na1 and three Na2 atoms in a mono-

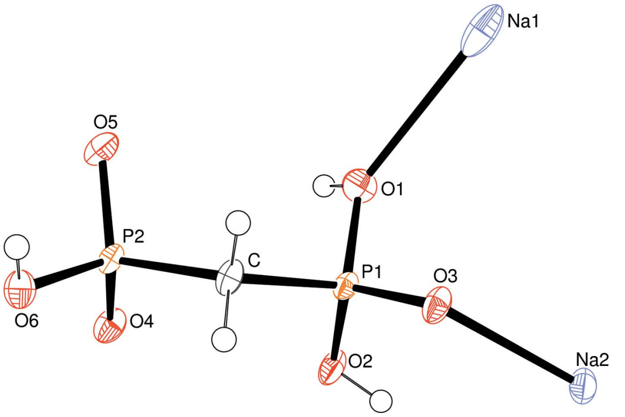


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids (arbitrary spheres for H atoms).

dentate mode and to one Na1 atom in a bidentate fashion. The values for the bond lengths and angles in (I) compare well with those reported in the literature (Serre & Ferey, 2001).

It is evident from the data in Table 2 that there are hydrogen-bonding interactions between diphosphonate moieties. The O1—H1 and O6—H6 groups of one diphosphonate moiety form hydrogen bonds with those O atoms formally double-bonded to P atoms, namely O3 and O4. Furthermore, O2—H2 is strongly hydrogen-bonded to atom O5.

Experimental

Compound (I) was synthesized, on a scale of 0.5–1.0 g, by evaporating aqueous solutions of stoichiometric mixtures of methylenediphosphonic acid (Lancaster Synthesis) and Na_2CO_3 (SD Fine Chemicals, India). Slow evaporation at room temperature led to the formation of (I) as colourless block-shaped crystals. However, evaporation over a steam bath yielded the same product in the polycrystalline form. The yield was almost quantitative. Elemental analysis, found: C 6.11, H 2.62%; $CH_5NaO_6P_2$ requires: C 6.07, H 2.55%. The observed X-ray powder pattern agrees with that simulated on the basis of a single-crystal X-ray structure using *LAZY-PULVERIX* (Yvon *et al.*, 1977), indicating the single-phase nature of the sample. IR data were measured using a Bruker IFS 66V FT–IR spectrometer between 400–4000 cm^{-1}. The C—H stretching vibrations of the methylenediphosphonate group are observed around 2970 and 2920 cm^{-1} (Minimol *et al.*, 2003), whereas their bending vibrations are seen at 1380 cm^{-1}. The peaks in the region 1200–1000 cm^{-1} are due to P—O streching vibrations and the O—P—O bending vibrations are found in the region 540–410 cm^{-1} (Rao *et al.*, 2004).

Crystal data

$[Na(CH_5O_6P_2)]$
$M_r = 197.98$
Monoclinic, $P2_1/n$
$a = 8.1041\ (14)$ Å
$b = 8.139\ (3)$ Å
$c = 9.7289\ (8)$ Å
$\beta = 99.860\ (10)^\circ$
$V = 632.2\ (2)$ Å^3
$Z = 4$
$D_x = 2.080$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.73$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
$0.30 \times 0.20 \times 0.20$ mm

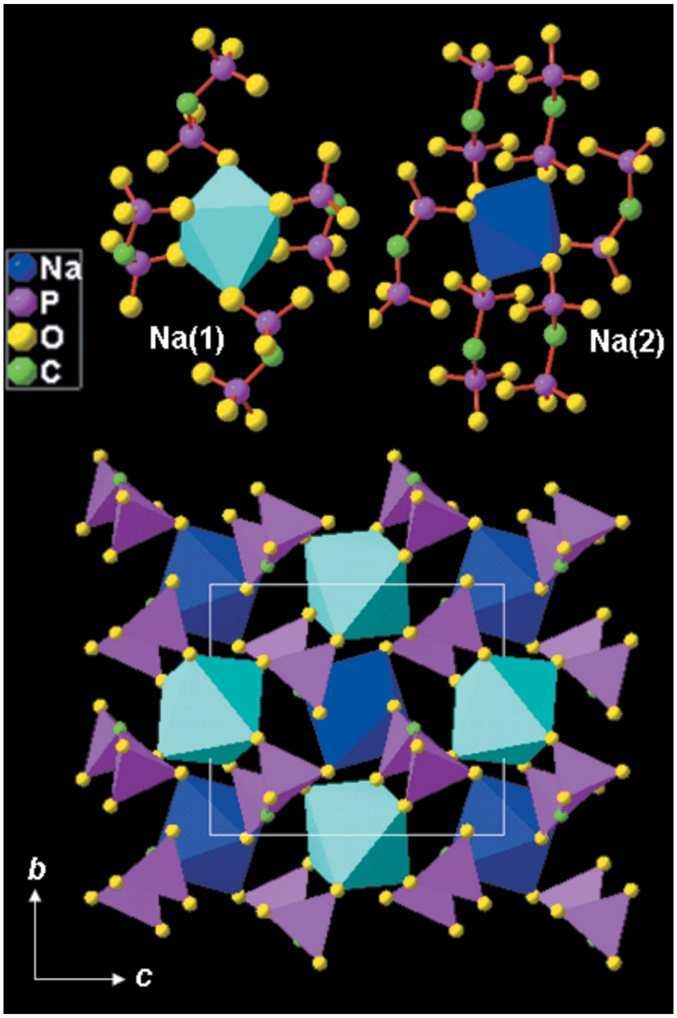


Figure 2
(Top) The coordination environments of atoms Na1 and Na2. (Bottom) A polyhedral representation of the unit cell of (I).

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan North *et al.* (1968)
$T_{min} = 0.716$, $T_{max} = 0.865$
1180 measured reflections
1112 independent reflections
1088 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.0^\circ$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 9$
$l = -11 \rightarrow 0$
2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.078$
$S = 1.24$
1112 reflections
105 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.6147P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.210 (9)

Table 1
Selected bond lengths (Å).

Na1—O4^{i}	2.3338 (16)	P1—O1	1.5570 (16)
Na1—O2^{i}	2.3843 (16)	P1—O2	1.5360 (16)
Na1—O1	2.7112 (17)	P1—O3	1.5047 (16)
Na2—O3	2.3197 (15)	P2—O4	1.5046 (17)
Na2—O5^{i}	2.3488 (17)	P2—O5	1.5273 (17)
Na2—O6^{ii}	2.5162 (16)	P2—O6	1.5640 (16)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{iii}	0.82	1.73	2.552 (2)	177
O2—H2···O5^{iv}	0.82	1.67	2.487 (2)	172
O6—H6···O4^{v}	0.82	1.71	2.526 (2)	175

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

All H atoms were located in difference maps. The P—OH H atoms were repositioned in idealized locations (O—H = 0.82 Å) and refined as riding. The methylene H atoms were freely refined.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *ORTEP3* (*WinGX*; Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge the financial support (Project No. 98/37/29/BRNS) received from the Board of Research in Nuclear Sciences, Government of India. We thank the Department of Chemistry, IIT Bombay, Mumbai, for the single-crystal X-ray data.

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