Ethylenediammonium disodium (1-hydroxyethylidene)diphosphonate tetrahydrate, [NH3(CH2)2NH3]Na2(hedp)·4H2O

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean $\sigma(C-C) = 0.004$ Å
R factor = 0.026
wR factor = 0.064
Data-to-parameter ratio = 9.3

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

The title structure, $C_2H_{10}N_2{}^{2+}\cdot2Na^+\cdot C_2H_4O_7P_2{}^{4-}\cdot4H_2O$ or $(NH_3CH_2CH_2NH_3)Na_2(hedp)\cdot4H_2O$ (SDP-2) (hedp = 1-hydroxyethylidenediphosphonate), contains one-dimensional anionic sodium–hedp chains which are connected by N—H···O and O—H···O hydrogen bonds. There are two crystallographically independent P atom environments.

Comment

Hydroxyethane-1,1-diphosphonic acid (H_4hedp), which has a characteristic P—C—P linkage, finds applications in biomedical areas, water treatment, ion exchange and lipophilic solvent extraction (Francis *et al.*, 1969; Jurisson *et al.*, 1993). Recently, owing to its versatile coordination abilities with metal ions, the compound has been introduced into the field of materials and used as a polydentate ligand to construct novel structures with special properties (Serezhkin *et al.*, 2000; Sergienko, 2000; Nash *et al.*, 1998). Hedp possesses seven active O atoms, so, at most, it can serve as a heptadentate ligand. Furthermore, the CH_3 and OH groups attached to the organic tether of hedp provide not only steric hindrance, but also a possible hydrophobic or hydrophilic environment which may be important in the self-assembly of some metal diphosphonates.

(I)
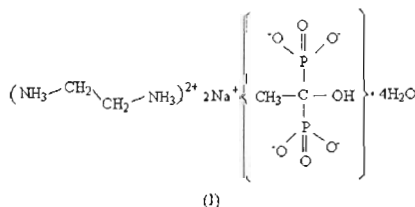
More recently, many efforts have been devoted to synthesizing open-framework metal–hedp compounds. The idea was highlighted by the studies on Sn_2(hedp) (Zapf *et al.*, 1996). Attempting to obtain novel structures, Zheng *et al.* (2000, 2002), using different organic amines as the template, synthesized several metal–hedp compounds with different structures (see also Song *et al.*, 2001). The authors attributed the structural differences among the compounds to the effect of the templates employed. The smaller size template $NH_2CH_2CH_2NH_2$ (en) directed the formation of a linear single chain compound, while the larger size templates such as $NH_2(CH_2)_m NH_2$ ($m = 4, 5, 6$) directed the formation of anionic double chains which were held together by strong hydrogen bonds to form three-dimensional channels. The use of organic amines as templates in the above synthetic process is relatively new; this not only diversifies the members of the family but
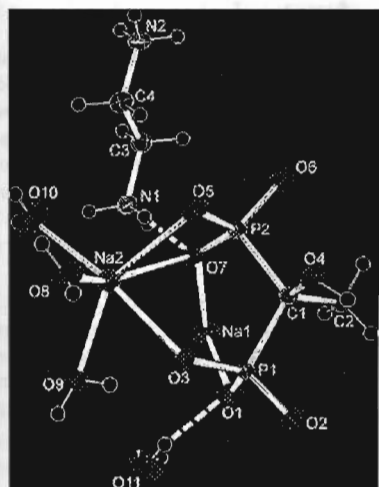
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Figure 1
The asymmetric unit of SDP-2, with the atomic labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen-bonding interactions.
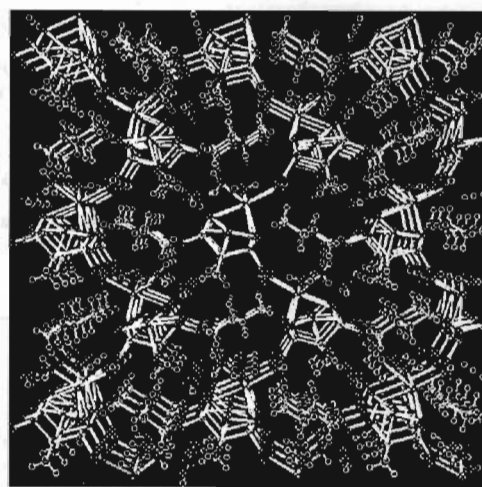

Figure 2
SDP-2 structure viewed along [010]. Displacement ellipsoids are drawn at the 60% probability level. Key: C atoms, gray; H atoms, white; N atoms, yellow; P atoms, green; Na atoms, red; O atoms, blue).

also adds a promising direction for future studies of the compounds.

In the present paper, we describe the synthesis and crystal structure of a new member of the metal–hedp series, $(NH_3CH_2CH_2NH_3)Na_2(hedp)\cdot4H_2O$ (designated as SDP-2, SDP is sodium diphosphonate), (1).

The fundamental building units of SDP-2 are the extended one-dimensional anionic $[Na_2(hedp)(H_2O)_3]^{2-}$ chains along the *b* axis; these are charge-balanced by enH_2^{2+} cations and linked together by hydrogen bonds (Figs. 1 and 2). Within a chain, two kinds of Na atom environment are found. The Na1 atom links with the hedp ligand through atoms O1 and O7 from one ligand and O3[i], O4[i] and O5[i] [symmetry code: (i) *x*, 1+*y*, *z*] from another neighboring ligand. By contrast, there are three bonds from water molecules (O8, O9 and O10) and three bonds from the hedp ligand through O3, O5 and O7 contributing to the coordination of Na2. For the two tetra-hedrally coordinated P atoms in the ligand, there are two pendant P=O bonds, namely P1=O2 and P2=O6, with lengths 1.5231 (19) and 1.514 (2) Å, respectively. In comparison with the P=O bond lengths in H4hedp and other metal–hedp compounds, the distance is greater; this can be explained by the fact that there are strong hydrogen bonds between P=O and enH_2^{2+}. Here hedp acts as a pentadentate ligand, bridging the Na atoms through four ionized O(P) atoms of the two diphosphonate groups and the protonated O(C) atom of the hydroxyl group. The torsion angles for O2−P1−C1−P2 and O6−P2−C1−P1 are −166.84 (12) and −166.68 (15)°, respectively. In structural contrast between SDP-2 and another disodium 1-hydroxylidenediphosphonate tetra-hydrate (Barnett & Strickland, 1979), the effect of ethyl-enediamine on tailoring the structure of the sodium 1-hydroxylidenediphosphonate is obvious. Between the chains, protonated enH_2^{2+} acts as a charge-compensating cation and also bridges the chains through N−H···O hydrogen bonds. Three coordinated water molecules (O8, O9 and O10) and one

uncoordinated water molecule (O11) also contribute to the hydrogen-bonding motif (see Table 2). These strong hydrogen bonds help stabilize the crystal structure.

Experimental

All starting materials were analytically pure and were used without further purification. SDP-2 was prepared by the following method. $Na_4C_2H_4O_7P_2$, NH4F (ammonium fluoride), H2O (deionized water) and $C_4H_8O_2$ (dioxane), in a 1:0.2:80:2 molar ratio, were stirred at ambient temperature in a plastic container. Ethylenediamine was added dropwise to the mixture until a pH of 10 was achieved. Stirring was continued until a homogeneous white gel formed. The container was covered with a watch glass, and left undisturbed at ambient temperature. After two weeks, transparent colorless crystals began to form. The purity of SDP-2 was verified by elemental analysis: calculated for $C_4H_{22}N_2Na_2O_{11}P_2$ (wt%): C 12.57, H 5.81, N 7.33, Na 12.03, P 16.21; found: C 11.90, H 4.73, N 7.07, Na 11.85, P 15.30. FT–IR (KBr pellet, ν cm^{-1}: 3259, 3103, 2993, 2988, 2130, 1719, 1648, 996, 955, 885, 806, 733. ^{13}C CP/MAS NMR (external reference: DSS, δ p.p.m.): 22.8 (CH3), 36.7 (CH2CH2), and 72.1 (=C); ^{31}P MAS NMR (external reference: 85% H3PO4, δ p.p.m.): 20.1 and 17.9.

Crystal data

$C_2H_{10}N_2^{2+}\cdot2Na^+\cdot C_2H_4O_7P_2^{4-}\cdot4H_2O$	Mo *Kα* radiation
$M_r = 382.16$	Cell parameters from 2203
Orthorhombic, $Pna2_1$	reflections
$a = 20.966$ (7) Å	$\theta = 1.9$–25.0°
$b = 5.8928$ (18) Å	$\mu = 0.41$ mm^{-1}
$c = 11.871$ (4) Å	$T = 293$ (2) K
$V = 1466.6$ (8) Å^3	Block, colorless
$Z = 4$	0.20 × 0.10 × 0.10 mm
$D_x = 1.731$ Mg m^{-3}	

Data collection

Bruker SMART CCD diffractometer	2203 independent reflections
	2021 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.025$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SADABS*; Sheldrick, 1996)	$h = -24 \rightarrow 22$
$T_{min} = 0.922$, $T_{max} = 0.960$	$k = -7 \rightarrow 4$
5700 measured reflections	$l = -12 \rightarrow 14$

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State Key

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o{}^2) + (0.0395P)^2]$	
$R[F^2 > 2\sigma(F^2)] = 0.026$		where $P = (F_o{}^2 + 2F_c{}^2)/3$	
$wR(F^2) = 0.064$		$(\Delta/\sigma)_{max} = 0.001$	
$S = 1.06$		$\Delta\rho_{max} = 0.27$ e Å^{-3}	
2203 reflections		$\Delta\rho_{min} = -0.31$ e Å^{-3}	
236 parameters		Absolute structure: Flack (1983),	
H-atom parameters constrained		1217 Friedel pairs	
		Flack parameter = −0.10 (10)	

Table 1
Selected geometric parameters (Å, °).

Na1—O1	2.312 (2)	P1—O2	1.5231 (19)
Na1—O7	2.316 (2)	P1—O1	1.5247 (19)
Na1—O5^i	2.348 (2)	P1—C1	1.855 (3)
Na1—O4^i	2.414 (3)	C1—O4	1.452 (3)
Na1—O3^i	2.553 (2)	C1—C2	1.522 (4)
Na2—O10	2.269 (3)	C1—P2	1.862 (3)
Na2—O9	2.351 (2)	P2—O6	1.514 (2)
Na2—O5	2.386 (2)	P2—O7	1.518 (2)
Na2—O8	2.399 (3)	P2—O5	1.5188 (19)
Na2—O8	2.418 (2)	N1—C3	1.477 (4)
Na2—O7	2.706 (3)	N2—C4	1.485 (4)
P1—O3	1.5219 (19)	C3—C4	1.521 (4)
O3—P1—O2	112.43 (11)	O4—C1—P2	102.90 (16)
O3—P1—O1	112.36 (11)	C2—C1—P2	110.51 (19)
O2—P1—O1	110.82 (11)	P1—C1—P2	114.33 (14)
O3—P1—C1	105.93 (11)	O6—P2—O7	113.40 (15)
O2—P1—C1	105.97 (12)	O6—P2—O5	112.44 (13)
O1—P1—C1	108.95 (11)	O7—P2—O5	110.53 (14)
O4—C1—C2	111.7 (2)	O6—P2—C1	105.57 (12)
O4—C1—P1	107.07 (17)	O7—P2—C1	106.62 (11)
C2—C1—P1	110.14 (18)	O5—P2—C1	107.83 (11)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1C⋯O7	0.92 (3)	1.80 (3)	2.689 (3)	160 (3)
O11—H11B⋯O1	0.86 (3)	1.99 (3)	2.804 (3)	158 (3)
N1—H1A⋯O5^i	0.89 (3)	1.90 (3)	2.768 (3)	163 (3)
N1—H1B⋯O6^{iii}	0.89 (4)	1.98 (4)	2.850 (4)	165 (3)
N2—H2A⋯O2^{iii}	0.91 (4)	1.76 (4)	2.669 (3)	177 (3)
N2—H2B⋯O1^{iv}	0.90 (3)	1.91 (3)	2.781 (3)	163 (3)
N2—H2C⋯O8^v	0.89 (4)	2.54 (4)	3.199 (4)	131 (3)
O4—H4⋯O11^{vi}	0.86 (4)	1.83 (4)	2.686 (3)	172 (3)
O8—H8A⋯O9^{vii}	0.85 (2)	2.04 (3)	2.869 (3)	165 (3)
O8—H8B⋯O6^{viii}	0.85 (2)	1.83 (3)	2.664 (3)	165 (3)
O9—H9B⋯O2^{ix}	0.86 (3)	1.80 (3)	2.653 (3)	175 (3)
O10—H10A⋯O6^{viii}	0.84 (3)	2.25 (2)	2.957 (4)	143 (3)
O10—H10B⋯O6^{ii}	0.85 (3)	2.31 (2)	3.099 (4)	155 (3)
O11—H11A⋯O3^i	0.85 (2)	1.88 (3)	2.668 (3)	154 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (v) $\frac{3}{2} - x, \frac{1}{2} + y, z - \frac{1}{2}$; (vi) $1 - x, 1 - y, z - \frac{1}{2}$; (vii) $x, y - 1, z$; (viii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (ix) $1 - x, 1 - y, \frac{1}{2} + z$.

H atoms of the hydroxy and protonated amino groups were in difference Fourier maps and were not incorporated in the ment. H atoms of methyl and methylene groups were plac geometrically calculated positions and refined with a riding m with bond distances constrained to 0.96 and 0.97 Å, respecti isotropic displacement parameters set at $1.5U_{eq}$ (1.2 for methyle the parent atoms. All water H atoms were refined with bond dist restrained to 0.89–0.92 Å, and isotropic displacement parameter at $1.5U_{eq}$ of the parent atoms.

Data collection: *SMART* (Siemens, 1996); cell refinem *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SHELX* (Sheldrick, 2001); program(s) used to solve structure: *SHELX* (Sheldrick, 1997); program(s) used to refine structure: *SHELX* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used prepare material for publication: *SHELXTL*.

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