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Trisodium Trimetaphosphimate Monohydrate

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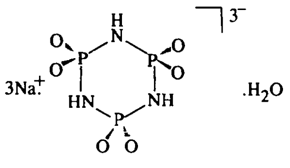
Abstract

The trimetaphosphimate anion $(PO_2NH)_3^{3-}$ in trisodium *cyclo*-tri-μ-imido-triphosphate monohydrate, $Na_3(PO_2NH)_3.H_2O$, exhibits a chair conformation. Two trimetaphosphimate rings are linked to one another by six N—H···O hydrogen bonds forming pairs. These units are interconnected by O—H···O hydrogen bonds through water molecules forming columns.

Comment

In contrast to the well known structural chemistry of trimetaphosphates (Durif, 1995), only very few structural details about trimetaphosphimates are known despite the fact that many salts of trimetaphosphimic acid were known more than 100 years ago (Stokes, 1895). These compounds have been mainly characterized by IR spectroscopy (Pustinger, Cave & Nielsen, 1959) and powder diffraction (Herzog & Nielsen, 1958). In contrast to $H_3(PO_2NH)_3.2H_2O$ and $(NH_4)H_2(PO_2NH)_3.CH_3OH$, where the P–N rings show a distorted boat conformation (Olthof, Migchelsen & Vos, 1965), the title compound, (I) (Fig. 1), $Na_3(PO_2NH)_3.4H_2O$ and $(NH_4)_3(PO_2NH)_3.H_2O$ exhibit distorted chair conformations (Attig & Mootz, 1976; Stock & Schnick, 1996).



(I)

As may be seen from the bond lengths and valence angles, the phosphimate ring in $Na_3(PO_2NH)_3.H_2O$ exhibits approximate $3m$ symmetry. Whereas in $(NH_4)_3(PO_2NH)_3.H_2O$ and $Na_3(PO_2NH)_3.4H_2O$, three-dimensional networks of $(PO_2NH)_3^{3-}$ anions and water molecules are formed by N—H···O and O—H···O hydrogen bonds, in $Na_3(PO_2NH)_3.H_2O$, rings are linked pairwise to one another by six N—H···O bonds [N···O 2.964 (2), 3.053 (2) and 3.121 (2) Å]. These units are

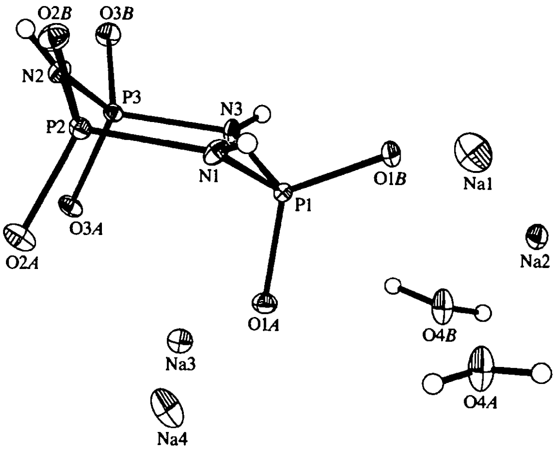


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids. H atoms are drawn as small circles of arbitrary size.

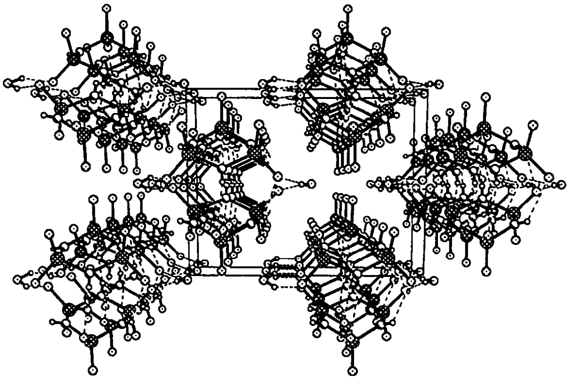


Fig. 2. View along [001] of the crystal packing of the trimetaphosphimate rings and water molecules illustrating the hydrogen bonds. The sodium ions have been omitted for clarity.

interconnected by water molecules through O—H···O hydrogen bonds [O···O 2.689 (2) and 2.720 (2) Å], thereby forming columns (Fig. 2). The sodium ions are approximately octahedrally coordinated by six O atoms from the phosphimate groups and from the water molecules [Na···O 2.282 (2)–2.984 (2) Å].

Experimental

The starting material, $Na_3(PO_2NH)_3.4H_2O$, was obtained according to Nielsen & Morrow (1960) by reaction (12 h, 323 K) of 3 g $Na(OOCCH_3).3H_2O$ in 48 ml water with 6 g $(PNCl_2)_3$ in 24 ml dioxane. Whereas the authors claim the synthesis of (I) under these conditions, $Na_3(PO_2NH)_3.4H_2O$ is formed. Sodium trimetaphosphimate monohydrate was prepared by a method similar to that of Stokes (1896); single crystals of (I) of up to 5 mm in length were grown by vapour diffusion of CH_3CH_2OH at 363 K into a 3×10^{-4} *M* aqueous solution of $Na_3(PO_2NH)_3.4H_2O$. These crystals are stable in air under ambient conditions. According to DSC measurements, decomposition starts at approximately 450 K with evolution of NH_3 and H_2O.

Crystal data

$Na_3(PO_2NH)_3.H_2O$
$M_r = 320.95$
Monoclinic
$C2$
$a = 9.8797 (7)$ Å
$b = 12.2119 (8)$ Å
$c = 7.6464 (6)$ Å
$\beta = 104.394 (6)°$
$V = 893.58 (11)$ Å^3
$Z = 4$
$D_x = 2.386$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 69 reflections
$\theta = 5.41–17.43°$
$\mu = 0.836$ mm^{-1}
$T = 173 (2)$ K
Column
$0.26 \times 0.08 \times 0.06$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical *via* ψ scans using *XSCANS* (Siemens, 1994) and *SHELXTL-Plus* (Sheldrick, 1994)
$T_{min} = 0.866$, $T_{max} = 0.951$
5209 measured reflections
2616 independent reflections

2259 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0367$
$\theta_{max} = 30°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 17$
$l = -10 \rightarrow 10$
3 standard reflections every 97 reflections intensity decay: 5.24%

Refinement

Refinement on F^2
$R(F) = 0.0311$
$wR(F^2) = 0.0663$
$S = 1.031$
2616 reflections
152 parameters
H atoms were refined using a riding model, starting from Fourier coordinates
$w = 1/[\sigma^2(F_o^2) + (0.0311P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.34 (12)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P1	0.77111 (6)	0.61560 (8)	0.15493 (8)	0.00777 (12)
P2	0.64506 (9)	0.74470 (6)	−0.17148 (10)	0.0075 (2)
P3	0.63899 (9)	0.50337 (6)	−0.19318 (11)	0.0082 (2)
Na1	0.87932 (10)	0.62554 (14)	0.61559 (13)	0.0119 (2)
Na2	1	0.7710 (2)	0	0.0142 (4)
Na3	1	0.4687 (2)	0	0.0175 (5)
Na4	0.72100 (14)	0.41584 (10)	−0.5720 (2)	0.0186 (3)
O1*A*	0.9208 (2)	0.6179 (2)	0.1454 (2)	0.0103 (3)
O1*B*	0.7368 (2)	0.6037 (2)	0.3330 (2)	0.0120 (4)
O2*A*	0.7745 (3)	0.7624 (2)	−0.2368 (3)	0.0117 (5)
O2*B*	0.5343 (3)	0.8306 (2)	−0.2080 (3)	0.0125 (5)
O3*A*	0.7623 (3)	0.4839 (2)	−0.2697 (3)	0.0132 (5)
O3*B*	0.5215 (3)	0.4204 (2)	−0.2342 (3)	0.0118 (5)
O4*A*	1	0.7685 (3)	1/2	0.0154 (7)
O4*B*	1	0.4603 (3)	1/2	0.0188 (8)
N1	0.6920 (3)	0.7271 (2)	0.0529 (3)	0.0088 (5)
N2	0.5710 (2)	0.6269 (3)	−0.2573 (3)	0.0086 (4)
N3	0.6928 (3)	0.5092 (2)	0.0300 (3)	0.0098 (5)

Table 2. *Selected geometric parameters (Å, °)*

P1—O1*B*	1.490 (2)	P2—N2	1.673 (3)
P1—O1*A*	1.499 (2)	P2—N1	1.676 (3)
P1—N1	1.665 (3)	P3—O3*A*	1.496 (3)
P1—N3	1.682 (3)	P3—O3*B*	1.514 (2)
P2—O2*B*	1.492 (3)	P3—N3	1.658 (3)
P2—O2*A*	1.499 (3)	P3—N2	1.674 (3)
O1*B*—P1—O1*A*	119.83 (10)	N2—P2—N1	105.92 (13)
O1*B*—P1—N1	108.76 (13)	O3*A*—P3—O3*B*	117.99 (14)
O1*A*—P1—N1	108.38 (15)	O3*A*—P3—N3	109.0 (2)
O1*B*—P1—N3	105.46 (14)	O3*B*—P3—N3	105.98 (14)
O1*A*—P1—N3	107.9 (2)	O3*A*—P3—N2	109.61 (12)
N1—P1—N3	105.63 (10)	O3*B*—P3—N2	108.12 (14)
O2*B*—P2—O2*A*	118.87 (14)	N3—P3—N2	105.38 (13)
O2*B*—P2—N2	107.60 (14)	P1—N1—P2	124.3 (2)
O2*A*—P2—N2	108.64 (12)	P2—N2—P3	123.72 (12)
O2*B*—P2—N1	106.59 (14)	P3—N3—P1	127.0 (2)
O2*A*—P2—N1	108.49 (14)		

Since the title compound crystallizes in a polar space group, polar axis restraints were applied according to the method of Flack & Schwarzenbach (1988) and the absolute structure of the crystal used for the investigation was established as described by Flack (1983). Linear decay was observed during the data collection and a correction was included in the data reduction procedure using *SHELXTL-Plus* (Sheldrick, 1994). All H atoms were unambiguously located after the anisotropic refinement of all non-H atoms. The ω-scan width was 1.2°, with an ω-scan rate of 3.0° min^{-1}. The background to signal ratio was 0.5.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BM1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Strontium Metasilicate, $SrSiO_3$

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Abstract

Strontium silicon trioxide has been synthesized for the first time and its structure solved. It is isostructural with the germanium analogue $SrGeO_3$ reported by Hilmer [*Sov. Phys. Crystallogr.* (1963), **7**, 573–576], but the true symmetry is monoclinic, rather than hexagonal as reported earlier. The structure has alternate layers of ternary rings of SiO_4 groups and close-packed Sr atoms stacked along [001]. Viewed as a polytype, this compound has a six-layer structure and the calcium analogue α-$CaSiO_3$ [Yamanaka & Mori (1981). *Acta Cryst.* B**37**, 1010–1017] has a four-layer structure.

Comment

The title compound has been synthesized for the first time. Dornberger-Schiff (1962) discussed the symmetry of the analogous germanium compound $SrGeO_3$. Hilmer (1963) studied the structure of $SrGeO_3$ using a Weissenberg camera. He obtained the hexagonal lattice parameters $a = 7.29$, $c = 31.64$ Å and showed that the structure contained ternary rings of GeO_4 groups. In addition, he concluded that the structure was composed of alternating layers of $[Ge_3O_9]^{6-}$ rings and layers of Sr atoms. Nadezhina, Pobedimskaya, Ilyukhin & Belov (1981*a*,*b*) also studied $SrGeO_3$ and obtained the triclinic lattice parameters $a = 8.699$, $b = 9.935$, $c = 11.148$ Å, $\alpha = 106.04$, $\beta = 89.97$, $\gamma = 102.11°$. This structure also contained rings of GeO_4 groups. The configurations of the rings, however, were somewhat different from those in the study by Hilmer, and Nadezhina *et al.* stated that the different types of ternary rings in the two modifications of strontium metagermanate were undoubtedly the result of a difference in the structures of the cation layers. In addition, they called the form they had studied the low-temperature form (α'-$SrGeO_3$) and the form studied by Hilmer the high-temperature form (α-$SrGeO_3$).

Ito (1950) and Buerger & Prewitt (1961) discussed the analogous calcium compound $CaSiO_3$ (the high-pressure form). Trojer (1969) obtained the triclinic lattice parameters $a = 6.695$, $b = 9.257$, $c = 6.666$ Å, $\alpha = 86.5$, $\beta = 76.13$, $\gamma = 70.38°$ and solved its structure. He concluded that the basic features of this structure were irregular layers of Ca atoms, which were interconnected by pairs of Ca atoms, and Si_3O_9 rings, which were located in the remaining space between the layers. Yamanaka & Mori (1981) studied the structure of α-$CaSiO_3$ (pseudowollastonite) from the viewpoint of polytypism. In their definition, a layer comprises one layer of the ternary rings plus one layer of CaO_8 polyhedra. They concluded that α-$CaSiO_3$ has a four-layer structure and the form of $SrGeO_3$ studied by Hilmer has a six-layer structure.

The symmetry of the title compound, $SrSiO_3$, was found to be different not only to that of the form of $SrGeO_3$ studied by Hilmer but also to that of the form of $SrGeO_3$ studied by Nadezhina *et al.* $SrSiO_3$, however, is almost isostructural with the form of $SrGeO_3$ studied by Hilmer for two reasons. Firstly, $SrSiO_3$ has a pseudo-hexagonal cell which corresponds to the cell given by Hilmer. Secondly, all of the reflections observed by Hilmer can be indexed on the basis of the present monoclinic cell. On the contrary, the structure of $SrGeO_3$ reported by Nadezhina *et al.* is different. It can be concluded that there are two forms of $SrGeO_3$, but only one form of $SrSiO_3$ is known so far.

The arrangement of the ternary rings of SiO_4 groups and SrO_8 polyhedra is shown in Fig. 1. The polyhedron around Sr(1) is very irregular, but that around Sr(2) can be regarded as a distorted hexagonal bipyramid, with O(1) on either side of the hexagon. The SrO_8 polyhedra form a close-packed layer like the olivine structure. The layers of the ternary rings of SiO_4 groups and the layers of SrO_8 polyhedra are shown in Fig. 2. They are stacked