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Disorder in the Structure of Trisodium Phosphorothioate Dodecahydrate*

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Abstract

Na₃PO₃S·12H₂O crystallizes in the trigonal space group $R\bar{3}c$ with $a = 9.061(2)$, $c = 34.34(2)$ Å (hexagonal axes), $Z = 6$, $V = 2441.6$ Å³, $D_c = 1.612$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 0.45$ mm⁻¹, $F(000) = 1248$. Final $R = 0.051$ for 326 independent observed reflections. The structure consists of discrete (PO₃S)³⁻ anions and (Na₃)³⁺(H₂O)₁₂ groups. All Na, P and S atoms lie on the unique axis. Hydrogen bonds involving all water molecules link the cation complexes both directly and through water–anion interactions. The (PO₃S)³⁻ anions are disordered with equal occupancy over two orientations related by the point symmetry $3C_2$. Evaluation of anion thermal parameters as well as low-temperature photographic diffraction data suggests that the disorder is static.

Introduction

The phosphorothioate anion has been the subject of a number of diverse studies. These have included the anion's role as a reducing agent (Neumann, Steinberg & Katchalski, 1965), a proposed phosphorylating agent of primordial nucleotides (Slabaugh, Harvey & Nagyvary, 1974) and its use in the preparation and study of nucleoside phosphorothioates (Burgers & Eckstein, 1979; Markham & Reed, 1978). Despite this,

crystallographic information on the anion and its salts has been limited to space group and unit-cell data (Palazzi, 1973; Elias, 1957). Thus a study was undertaken to determine the complete structure of the title compound.

Experimental

Small colorless crystals were grown at room temperature by evaporation from an aqueous solution of the title compound, obtained from Alfa Products. Crystals decomposed in air, presumably due to the loss of H₂S (Yasuda & Lambert, 1957). Each crystal studied was thus sealed in a 1.0 mm diameter quartz capillary tube containing a wick saturated with mother liquor. Precession photographs showed a rhombohedral lattice with Laue symmetry $\bar{3}m1$. Indexing of the corresponding hexagonal lattice showed reflection conditions hkl ; $-h + k + l = 3n$ and $h\bar{h}l$; $l = 2n$, indicating space group $R\bar{3}c$ (No. 167) or $R3c$ (No. 161). These were not in agreement with Elias (1957) whose choice of possible space groups as $R\bar{3}m$, $R32$ or $R3m$ suggests that the c glide was overlooked.

Cell dimensions and intensity data were collected from a crystal of approximate dimensions 0.23 × 0.18 × 0.11 mm with a Picker four-circle diffractometer using Zr-filtered Mo $K\alpha$ radiation. The crystal was mounted with the b^* (hexagonal) axis parallel to the ϕ axis of the instrument. Lattice constants were determined by least-squares refinement of 2θ angles from ten independent reflections in the range $2\theta = 45$ – 50° where the a_1 – a_2 doublet is resolved (λ for Mo $K\alpha_1 =$

* Also known as trisodium monothiophosphate dodecahydrate.

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0.70926 Å). These are in good agreement with those of Elias (1957) and Palazzi (1973). Reflections were measured to $2\theta = 55^\circ$ using the 2θ scan method with a scan rate of $1^\circ (2\theta) \text{ min}^{-1}$ and a scan base width of $1.2^\circ (2\theta)$, the actual range of each scan being adjusted for dispersion. Three reference reflections measured every 100 observations indicated a 4% decline in intensity over the course of the data collection. A correction was made by scaling the data with a polynomial fit of the averaged reference intensities as a function of reflection number. 3615 reflections were measured in the $h, k, +l$ hemisphere. Equivalent reflections were averaged to give 637 unique reflections of which 326 had intensities greater than $2.5\sigma(I)$. Lorentz and polarization factors were applied but no correction for absorption was made.

Structure determination

Initial coordinates for the Na and water O atoms were obtained from the Patterson map. Subsequent three-dimensional Fourier and difference maps showed two sets of equal-weight peaks suggesting two alternative orientations for the $(\text{PO}_3\text{S})^{3-}$ anion. Although Wilson statistics produced ambiguous results, refinements of both ordered and disordered structures in $R3c$ were unsatisfactory. The ordered structure yielded a conventional R value of approximately 0.15 and failed to converge. The disordered structures, with variable occupancies of the two anion sites, lowered R to approximately 0.07 but yielded large oscillations in coordinate shifts and several nonpositive-definite temperature factors. The disordered model, with equal occupancy of both sites by half-weighted anions, was successfully refined in $R3c$. Full-matrix least-squares techniques were used, the function minimized being $\sum w(|F_o| - |F_c|)^2$. Weights were calculated according to $w = [2I/|F_o|\sigma(I)]^2$ where I is the peak count and $\sigma(I)$ the standard deviation obtained from counting statistics. Anisotropic refinement of all non-H atoms yielded a conventional $R = 0.073 \{R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.051\}$ for the 326 unique reflections with intensities $>2.5\sigma(I)$. All shift/e.s.d. ratios were <0.01 and all temperature factors positive-definite. Subsequent difference maps showed unambiguous peaks corresponding to the four H atoms in the asymmetric unit. Further refinement including H atoms with isotropic temperature factors lowered R to 0.051 ($R_w = 0.039$) although shift/e.s.d. ratios for H-atom parameters remained ≈ 1 . The final difference map was featureless except for two peaks ($0.24, 0.29 \text{ e } \text{Å}^{-3}$) at the two sodium sites and three symmetry-equivalent peaks ($0.21 \text{ e } \text{Å}^{-3}$) lying about the $\bar{3}$ axis in the plane of the phosphorothioate O atoms. The residual sodium peaks may have been due to the use of atomic scattering factors for the Na^+ ion. The location of the

second set of residual peaks suggested an additional disorder of the $(\text{PO}_3\text{S})^{3-}$ O atoms due to rotation of the anion about the P–S bond. This would be consistent with findings from ESR studies of the λ -irradiated salt (Picone, Raynor & Ward, 1976). However, attempts at refinement of this model were unsuccessful and indicated that this type of disorder, if present, is very slight.

Atomic scattering factors for P, S, O, O^- and Na^+ were those of Cromer & Mann (1968) and for H those of Stewart, Davidson & Simpson (1965). Anomalous-scattering corrections for P, S and Na were those of Cromer & Liberman (1970). Final atomic coordinates and temperature factors are given in Table 1 and selected bond lengths and angles in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36563 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and isotropic thermal parameters for $\text{Na}_3\text{PO}_3\text{S} \cdot 12\text{H}_2\text{O}$*

The e.s.d.'s of the last significant figures are given in parentheses in all tables. n is the occupancy factor.

$$\text{For non-H atoms } B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	n	x	y	z	B_{eq} or B (Å ²)
Na(1)	1	0	0	0	3.1 (1)
Na(2)	1	0	0	0.09249 (9)	2.7 (1)
P	0.5	0	0	0.2295 (2)	1.9 (1)
S	0.5	0	0	0.2875 (2)	5.0 (2)
O	0.5	0.1740 (10)	0.0434 (10)	0.2139 (2)	4.8 (4)
OW(1)	1	0.1970 (6)	0.1978 (5)	0.0466 (1)	3.4 (1)
OW(2)	1	0.2184 (7)	0.0065 (6)	0.1320 (1)	4.0 (2)
H(1)	1	0.283 (6)	0.228 (7)	0.049 (1)	4.2 (13)
H(2)	1	0.188 (6)	0.284 (7)	0.047 (1)	7.8 (16)
H(3)	1	0.298 (6)	0.071 (6)	0.129 (1)	4.8 (15)
H(4)	1	0.200 (7)	0.015 (7)	0.156 (1)	7.1 (13)

Table 2. *Interatomic distances (Å) and angles (°) in the phosphorothioate anion and sodium octahedra*

For superscripts see Table 3.

(a) $(\text{PO}_3\text{S})^{3-}$ anion			
P–S	1.992 (8)	P–O	1.519 (9)
S–P–O	110.6 (3)	O–P–O ¹	108.3 (4)
(b) $(\text{Na}_3)^{3+} (\text{H}_2\text{O})_{12}$ octahedra			
Na(1)–Na(2)	3.176 (4)	OW(1)–OW(1 ^b)	3.666 (6)
Na(1)–OW(1)	2.400 (3)	OW(1)–OW(2)	3.461 (6)
Na(2)–OW(1)	2.384 (4)	OW(1)–OW(2 ^b)	3.500 (6)
Na(2)–OW(2)	2.376 (6)	OW(2)–OW(2 ^b)	3.378 (11)
OW(1)–OW(1 ^b)	3.098 (6)		
OW(1)–Na(1)–OW(1 ^b)	80.4 (1)	OW(1)–Na(2)–OW(2 ^b)	94.7 (2)
OW(1)–Na(1)–OW(1 ^b)	99.6 (1)	OW(1 ^b)–Na(2)–OW(2)	173.4 (2)
OW(1)–Na(2)–OW(1 ^b)	81.1 (1)	OW(2)–Na(2)–OW(2 ^b)	90.6 (2)
OW(1)–Na(2)–OW(2)	93.3 (2)		

Discussion

The crystal structure is composed of discrete $(\text{PO}_3\text{S})^{3-}$ anions and $(\text{Na}_3)^{3+}(\text{H}_2\text{O})_{12}$ groups (Fig. 1). Each Na^+ cation lies on the $\bar{3}$ axis (hexagonal c axis) and is coordinated to six water O atoms, forming a finite chain of three face-sharing octahedra. The entire $(\text{Na}_3)^{3+}(\text{H}_2\text{O})_{12}$ group displays a center of symmetry at Na(1). Lone-pair orbitals of $\text{OW}(1)$ form ligands with Na(1) and Na(2). These lie in a plane which is approximately normal to the plane of the $\text{H}(1)\text{—OW}(1)\text{—H}(2)$ molecule and approximately bisects the $\text{H}(1)\text{—OW}(1)\text{—H}(2)$ angle. This water is thus of class 2 type *A*, according to the classification scheme for hydrate waters originally proposed by Chidambaram, Sequeira & Sikka (1964) (see also Albertsson & Elding, 1976, and references therein). Only one lone-pair orbital of $\text{OW}(2)$ forms a ligand with the Na(2) cation, the remaining orbital acting as a hydrogen acceptor (see below). The $\text{H}(3)\text{—OW}(2)\text{—H}(4)$ water molecule is thus of class 2 type *G*. Ligand geometry is similar to that observed in other hydrated sodium salts containing water molecules of these classes (Albertsson & Elding, 1976; Ferraris & Franchini-Angela, 1972).

The $(\text{PO}_3\text{S})^{3-}$ anion has threefold symmetry about the P—S bond, which is collinear with the $\bar{3}$ axis. The anion is disordered, with equal occupancy of both sites. Alternative orientations for each half-weighted anion are related by rotation about any one of the three equivalent diad axes normal to the P—S bond and convergent at the site $0,0,\frac{1}{4}$ (hexagonal axes). The

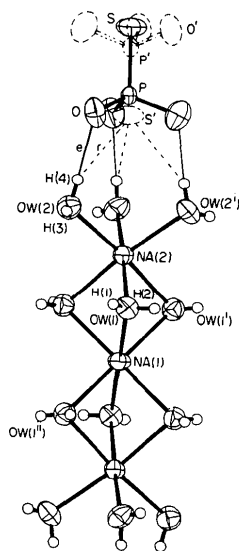


Fig. 1. $\text{Na}_3\text{PO}_3\text{S} \cdot 12\text{H}_2\text{O}$ formula unit viewed along the $\bar{3}$ (c) axis. Primed atoms indicate the alternative orientation for the disordered anion. Non-H atoms are represented by thermal ellipsoids at the 50% probability level. Thin solid and dashed lines are potential hydrogen bonds (see Table 3 for superscripts).

disorder thus satisfies the point symmetry $\bar{3}2$ and, through the action of the c glide, gives the structure an effective center of symmetry. P—S and P—O bond lengths and the S—P—O bond angle are similar to those observed in phosphoromonothioates in which the P—O rather than P—S linkages are thought to have the most π character, e.g. 2.00, 1.53 Å, 114° in $\text{NH}_4\text{POS}(\text{NH}_2)_2$; 2.05, 1.53 Å, 110° in $(\text{NH}_4)_2\text{PO}_2\text{S}(\text{NH}_2)$ and 2.01, 1.51 Å, 116° in $\text{Co}(\text{PhPSO})$ (Corbridge, 1974). The contents of the triply primitive hexagonal unit cell are shown in Fig. 2.

Hydrogen-bond distances and angles are shown in Table 3. O—H bond distances appear unreasonably short, suggesting inaccuracies in H-atom parameters greater than those implied by the e.s.d.'s. This is probably the result of well known systematic errors, especially in view of the limited number of reflections available for use in the refinement (Hamilton & Ibers, 1968). Nevertheless, bond geometries are reasonable and an unambiguous hydrogen-bonding scheme emerges (Fig. 2). $(\text{Na}_3)^{3+}(\text{H}_2\text{O})_{12}$ groups are directly linked by a long (2.806 Å) $\text{OW}(1)\text{—H}(2)\cdots\text{OW}(2)$ hydrogen bond. Each group forms two such bonds (t and t' in Fig. 3) with each of its six nearest neighbors. The $(\text{PO}_3\text{S})^{3-}$ anion sits in a cavity formed by 18

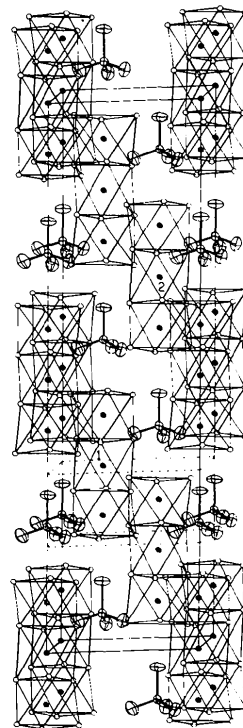


Fig. 2. Hexagonal unit-cell contents viewed along the c axis. Small shaded circles are sodium cations and small open circles are water O atoms. For clarity, anions are shown in one orientation only and H atoms are not shown. Atoms labeled 1 and 2 are located at centers $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$ and $\frac{2}{3}, \frac{2}{3}, \frac{2}{3}$ respectively. Dashed lines enclose the contents of the cell shown in projection in Fig. 3.

Table 3. *Interatomic distances (Å) and angles (°) in the water molecules and hydrogen bonds*

(a) Water geometries

OW(1)—H(1)	0.69 (5)	OW(2)—H(3)	0.67 (4)
OW(1)—H(2)	0.83 (7)	OW(2)—H(4)	0.85 (5)
H(1)—OW(1)—H(2)	104 (6)	H(3)—OW(2)—H(4)	104 (5)
Na(1)—OW(1)—Na(2)	83.2 (1)	Na(2)—OW(2)⋯H(2 ^v)	92 (1)

(b) Hydrogen bonds and sulfur contacts

1	2	3	4	1-3	2-3	∠1-2-3	1-4	2-4	∠1-2-4
OW(1 ^{iv})—H(2 ^{iv})⋯OW(2 ^v)				2.806 (8)	2.01 (7)	162 (4)	—	—	—
OW(1 ^{iv})—H(1 ^{iv})⋯O or S'				2.662 (11)	2.00 (4)	162 (6)	3.794 (5)	3.11 (5)	170 (5)
OW(2 ⁱⁱⁱ)—H(3 ⁱⁱⁱ)⋯O or S'				2.564 (8)	1.91 (4)	164 (8)	3.659 (5)	2.99 (4)	173 (7)
OW(2)—H(4)⋯O or S'				2.884 (9)	2.03 (5)	176 (5)	3.383 (7)	2.61 (6)	151 (5)

Superscripts indicate equivalent positions as follows: none x, y, z ; (i) $\bar{y}, x - y, z$; (ii) $y, \bar{x} + y, \bar{z}$; (iii) $\frac{2}{3} - x, \frac{1}{3} - y, \frac{1}{3} - z$; (iv) $\frac{1}{3} - x + y, -\frac{1}{3} + y, \frac{1}{3} + z$; (v) $\frac{2}{3} + y, \frac{1}{3} - x + y, \frac{1}{3} - z$; (vi) $\frac{1}{3} - x, -\frac{1}{3} - x + y, \frac{1}{3} - z$.

Primed atoms and bonds are related to unprimed atoms and bonds by the rotation diad parallel to a and passing through $0, 0, \frac{1}{2}$, *i.e.* $x', y', z' = x - y, y, \bar{z} + \frac{1}{2}$.

water molecules from the eight neighboring $(\text{Na}_3)^{3+}(\text{H}_2\text{O})_{12}$ groups, six of which are shown around the central anion in Fig. 3 (the remaining two neighboring groups lie directly above and below the anion and are not shown in this projection). The anion environment (hence the hydrogen-bonding scheme) is the same for either anion orientation, as the two orientations are related by the point symmetry of the anion site. Each phosphorothioate O atom acts as an acceptor in three hydrogen bonds (e in Fig. 1; f and g in Fig. 3), linking water oxygen donors from three neighboring $(\text{Na}_3)^{3+}(\text{H}_2\text{O})_{12}$ groups. Donor water O atoms are situated in a distorted tetrahedral arrangement around the anion oxygen, suggesting some degree

of sp^3 hybridization for this atom. The remaining nine potential hydrogen donors form a pocket around the S atom. Of these, only three symmetry-equivalent OW(2) atoms make close enough contact with the S atom (3.383 Å) to be considered as possible donors in OW(2)—H(4)⋯S hydrogen bonds (r in Fig. 1). However, the resulting tetrahedral environment around the S atom is quite distorted. The remaining six sulfur contacts are at distances of 3.659 (5) and 3.794 (5) Å. These waters contribute six H atoms which lie at approximately right angles to the P—S bond and probably do not engage in any bonding interactions with the S atom. When the anion is in the alternative orientation, they act as donors in the hydrogen bonds to the anion O atoms (f' and g' in Fig. 3).

The presence of orientational disorder raises the question of whether the disorder is static or dynamic. In this case static disorder implies that each phosphorothioate anion occupies only one of the two alternative orientations described above and does not reorient itself over the time course of the diffraction experiment. Dynamic disorder implies that each anion undergoes temperature-dependent rotational jumps from one orientation to the other. It is assumed that the time spent in each of the two orientations is large compared to that needed for the reorientation motion but small relative to the total time course of the diffraction experiment (Parsonage & Staveley, 1978). Dynamic disorder of this type has been demonstrated in hydrate salts, the temperature-dependent reorientation of the sulfate group in potassium alum offering one example (Eysel & Schumacher, 1977). Nevertheless, dynamic disorder is unlikely in the phosphorothioate structure. Rotation of the $(\text{PO}_3\text{S})^{3-}$ anion from one orientation to the other would not occur about an anion axis of symmetry. This unusual motion would require a 1.4 Å net shift in the P-atom center, a range of movement inconsistent with the

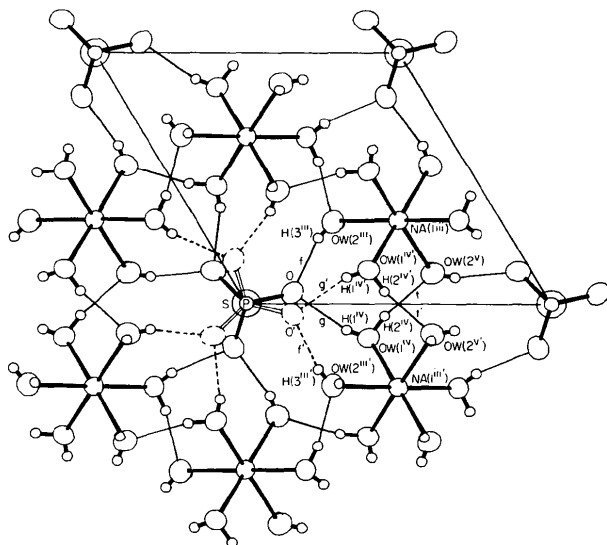


Fig. 3. Projection along [001] of the hexagonal unit-cell contents contained between $z = 0.17$ and $z = 0.33$ (see Fig. 2). The a axis is horizontal. The dashed anion is in the alternative orientation as in Fig. 1. S atoms are transparent. Thin solid and dashed lines are hydrogen bonds. See Table 3 for superscripts.

relatively small thermal parameters obtained for this atom. The largest phosphorus r.m.s. displacement is 0.18 (1) Å along the unique principal axis collinear with the P—S bond. The phosphorus r.m.s. displacement along the two symmetry-equivalent principal axes normal to the P—S bond is 0.14 (1) Å. As expected, the largest sulfur r.m.s. displacement, 0.28 (1) Å, occurs along the axes normal to the P—S bond. The displacement along the axis collinear with the P—S bond is 0.17 (1) Å. The greatest anion oxygen r.m.s. displacement is 0.30 (1) Å along a principal axis oriented at an angle of 86 (6)° with the P—O bond and 25 (6)° with the P—S bond, this motion being approximately normal to the P—O bond and approximately parallel to the S—P—O plane. Remaining oxygen displacements are 0.19 (3) and 0.23 (1) Å along axes oriented at angles of 76 (10) and 111 (8)° respectively with the P—S bond.

In an attempt to address the question of disorder type further, crystals of the hydrate were cooled to approximately 77 K and a series of precession photographs obtained. These were compared with photographs of the same crystals taken at room temperature both before cooling and after warming. Each crystal was mounted in a quartz capillary tube about the b^* (hexagonal) axis. The low-temperature photographs showed no change in possible space groups ($R3c$ or $R\bar{3}c$) and no measureable changes in lattice parameters or in intensities of reflections expected to be sensitive to reorientations of the anion. These findings do not exclude the possibility of a dynamically disordered structure at room temperature which either undergoes an ordering transition below 77 K or which freezes into a statically disordered structure at low temperature. However, it appears most likely that the observed disorder is static at room temperature.

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