

## Disorder of $\text{HPO}_4^{2-}$ and of Hydrogen Bonds in the Structure of $\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$

BY M. CATTI, G. FERRARIS AND G. IVALDI

*Istituto di Mineralogia Cristallografia e Geochimica 'G. Spezia' dell'Università di Torino, Via S. Massimo 24, 10123 Torino, Italy*

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$\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  crystallizes in space group  $C2/c$  with  $a = 15.718$  (5),  $b = 9.018$  (3),  $c = 12.769$  (3) Å,  $\beta = 121.39$  (2)°,  $Z = 4$ . The structure was refined to  $R = 0.030$  for 1565 counter reflexions; H atoms were located on difference maps. Close-packed (001) layers are built up by  $\text{Na}(\text{H}_2\text{O})_6$  coordination octahedra, one third of which are substituted by  $\text{PO}_4$  tetrahedra. The latter are twofold-disordered because of the higher symmetry of the site; through the acidic hydrogen bond the disorder is propagated to the water molecules, which are rotationally disordered around one O–H direction. Considerations based on the refinement, closeness to dehydration point and crystal chemistry suggest a dynamic disorder in which the hydrogen bonds play a major role.

### Introduction

Disodium hydrogenphosphate dodecahydrate is known in two phases, which crystallize from water solutions below 30°C ( $\beta$ ) and between 30 and 35°C ( $\alpha$ ) respectively (Pascal, 1966). The relevant physical and chemical data are often reported without reference to a specific phase; in such cases they should, presumably, be referred to the  $\beta$  phase, which corresponds to the commercial product and is isostructural with the unique  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  (Pascal, 1966). As part of an investigation of hydrogen bonding, particularly in various series of hydrates, the structural study of  $\beta\text{-Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  was undertaken, following that of  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  (Catti, Ferraris & Franchini-Angela, 1977); a specific aim in determining the structure of the title compound was to investigate the structural reasons for its very quick dehydration, e.g. possible interstitial water molecules.

### Experimental

The commercial product used for the measurements shows rounded crystals which are stable in aggregates or in sealed containers; in the open air they dehydrate within a few minutes to  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ . Weissenberg photographs and single-crystal diffractometry confirmed the monoclinic cell found by de Wolff (Pascal, 1966) with the least-squares-refined values ( $\lambda = 1.54178$  Å) given in the Abstract. Systematic absences, statistical tests on the intensities and morphology (Steinmetz, 1921) were consistent with the space group  $C2/c$ , even though preliminary structural considerations showed that an ordered structure was possible only in  $Cc$ .

Other data are:  $M_r = 358.157$ ,  $V = 1535.6$  Å<sup>3</sup>,  $D_m = 1.530$  [average of three values given by Pascal (1966)],  $D_c = 1.549$  g cm<sup>-3</sup>,  $Z = 4$ ,  $F(000) = 760$ ,  $\mu(\text{Mo } K\alpha) = 3.1$  cm<sup>-1</sup>.

Intensities were collected on a Philips PW 1100 automatic four-circle diffractometer from a spheroidal crystal (mean diameter about 0.5 mm) sealed in a Lindemann capillary tube. The measurement conditions were: Mo  $K\alpha$  radiation, graphite monochromator,  $\theta \leq 28^\circ$ ,  $\omega/2\theta$  scan,  $\Delta\omega = 1.70^\circ$ , scanning speed 0.035° s<sup>-1</sup>, background time 5 s on both sides of each peak, attenuating filter inserted for intensities higher than 60 000 counts s<sup>-1</sup>, three reference reflexions. After removal of 297 reflexions with  $|F_o|^2 \leq 2\sigma(|F_o|^2)$  1565 independent observations were left.\*

### Solution and refinement of the structure

Space group  $C2/c$  and  $Z = 4$  require the P tetrahedron to lie on a special position with consequent disorder of at least the acidic H. For that reason, and because of difficulties in obtaining a solution in  $C2/c$ , a solution was sought in  $Cc$  by comparison of results from *MULTAN* (Germain, Main & Woolfson, 1971) and from a Patterson function. Starting with the coordinates of P and of one Na, Fourier syntheses showed the complete set of non-hydrogen atoms. The structure turned out to be strongly centrosymmetric, except for the tetrahedral moiety; the full-matrix least-squares refinement converged normally by minimizing the

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33014 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

quantity  $\sum_i w_i |F_o - F_c|^2$ , following Rae's (1974) method for pseudosymmetric cases.

However, the presence of an exceptionally short hydrogen bond (Ferraris & Franchini-Angela, 1972) donated by a water molecule to an anionic oxygen [2.457 (5) Å, now 2.561 (3) Å], an unsatisfactory bond-strength balance (Brown, 1976; Brown & Wu, 1976) and the impossibility of locating at least one-half of the H atoms suggested a check for a disordered C2/c model. This model, with P on a twofold axis and occupation factors of 0.5 for the anionic O atoms, converged anisotropically (full-matrix least squares) to  $R = 0.049$ ; at the same stage of refinement, the ordered Cc model gave  $R = 0.084$ . A subsequent difference Fourier synthesis showed all the H atoms, including those with occupation factor 0.5 (Table 1). After a further refinement, where the positions of the H atoms were kept fixed, the final values of  $R$  and of the standard error of an observation were 0.030 and 0.97 respectively. Unitary weights were used, since the average values of  $\Delta^2$  for groups of reflexions  $vs |F_o|$  and  $\sin \theta$  were practically constant except for the groups of the weakest and of the strongest reflexions; an analysis of the function  $I_c/I_o = k(1 + gI_c)$  for secondary extinction showed no systematic effects.

Table 1. Fractional coordinates with significant figures of the e.s.d.'s in parentheses and occupation factors (o.f.) of the atoms

	x	y	z	o.f.
P	$\frac{1}{2}$	0.54766 (6)	$\frac{1}{2}$	1
Na	0.82878 (6)	0.55886 (9)	0.24214 (7)	1
O(1)	0.5758 (2)	0.4520 (3)	0.3560 (2)	0.5
O(2)	0.4818 (2)	0.4630 (3)	0.1305 (2)	0.5
O(3)	0.4019 (2)	0.5555 (3)	0.2456 (2)	0.5
O(4)	0.5403 (2)	0.6999 (2)	0.2510 (2)	0.5
W(1)	0.6604 (1)	0.4541 (1)	0.0983 (1)	1
W(2)	0.8868 (1)	0.4424 (1)	0.1195 (1)	1
W(3)	0.7799 (1)	0.7776 (2)	0.1216 (1)	1
W(4)	0.7762 (1)	0.6569 (2)	0.3778 (1)	1
W(5)	0.8898 (1)	0.3398 (2)	0.3683 (1)	1
W(6)	0.9898 (1)	0.6660 (2)	0.3776 (1)	1
H(1)	0.620	0.465	0.130	1
H(2)	0.915	0.360	0.155	1
H(3)	0.825	0.855	0.145	1
H(4)	0.715	0.635	0.350	1
H(5)	0.910	0.270	0.335	1
H(6)	1.010	0.760	0.370	1
H(7)	0.420	0.490	0.050	0.5
H(8)	0.625	0.485	0.015	0.5
H(8')	0.675	0.355	0.105	0.5
H(9)	0.840	0.425	0.035	0.5
H(9')	0.930	0.510	0.130	0.5
H(10)	0.730	0.810	0.120	0.5
H(10')	0.760	0.780	0.045	0.5
H(11)	0.785	0.750	0.385	0.5
H(11')	0.820	0.615	0.455	0.5
H(12)	0.935	0.345	0.440	0.5
H(12')	0.830	0.320	0.360	0.5
H(13)	1.030	0.580	0.370	0.5
H(13')	1.020	0.660	0.455	0.5

Scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1962) and, when not otherwise stated, the XRAY system (Stewart, Kundell & Baldwin, 1970) were used.

## Discussion

### Description of the structure

The  $\text{Na}^+$  ion coordinates the six independent water molecules, so as to form a fairly regular octahedron (Table 2);\* stoichiometry and coordination requirements are then satisfied without the sharing of O atoms between  $\text{Na}(\text{H}_2\text{O})_6$  and  $\text{PO}_4$  (Table 3) polyhedra, and without any interstitial water molecules. The structure is built up by pairs of centrosymmetric (001) layers of close-packed octahedra, one third of which are substituted by P tetrahedra (Fig. 1); such an arrangement is favoured by the presence of regular and isolated coordination polyhedra. Adjacent layers are tied together only by hydrogen bonding and, therefore, an easy (001) cleavage should be present even if not noted so far (possibly because of the quick deterioration of

\* A single (or no) figure in parentheses denotes an atom of the asymmetric unit; primed figures are used for alternative positions of disordered H atoms. A second figure, ranging from 2 to 8, is included for atoms in the positions  $x, y, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} + y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z; x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, z; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ . Roman numerals represent the following translations: (I) a; (II) 2a; (III) b; (IV) -b; (V) b - c; (VI) a - b; (VII) a + b; (VIII) 2a + b + c.

Table 2. Interatomic distances and O...Na...O angles in the Na coordination polyhedron

The e.s.d.'s are 0.002 Å and 0.1° for distances and angles respectively.

Na-W(1)	2.492 Å	
Na-W(2)	2.424	
Na-W(3)	2.371	
Na-W(4)	2.441	
Na-W(5)	2.410	
Na-W(6)	2.402	
Average	2.423	
W(1)-W(2)	3.428 Å	88.4°
W(1)-W(3)	3.399	88.7
W(1)-W(4)	3.553	92.1
W(1)-W(5)	3.606	94.7
W(6)-W(2)	3.463	91.7
W(6)-W(3)	3.369	89.8
W(6)-W(4)	3.360	87.9
W(6)-W(5)	3.308	86.9
W(5)-W(2)	3.286	85.6
W(5)-W(4)	3.407	89.2
W(3)-W(2)	3.466	92.6
W(3)-W(4)	3.478	92.6
Average	3.427	90.0
W(2)-W(4)	—	174.9
W(1)-W(6)	—	178.4
W(5)-W(3)	—	176.1

the compound). The P tetrahedron lies in the centre of the pseudo-hexagonal mesh of Na octahedra and, in order to satisfy in part this higher symmetry, is disordered over two positions related by the twofold axis on which P is placed.

#### Hydrogen bonding

The hydrogen-bonding scheme (Table 4), which has been determined unequivocally by locating all the H atoms, involves a large range of O...O distances (2.561–3.203 Å) and is influenced strongly by the close packing of octahedra, which plays a major role in

Table 3. *Interatomic distances and O–P–O angles in the P tetrahedron (e.s.d.'s for the angles are 0.1°)*

P–O(1)	1.522 (3) Å	
P–O(2)	1.594 (3)	
P–O(3)	1.517 (3)	
P–O(4)	1.510 (2)	
Average	1.536	
O(1)–O(2)	2.460 (3) Å	104.3°
O(1)–O(3)	2.514 (4)	111.7
O(1)–O(4)	2.516 (3)	112.2
O(2)–O(3)	2.523 (4)	108.4
O(2)–O(4)	2.511 (3)	108.0
O(3)–O(4)	2.507 (4)	111.9
Average	2.505	109.4

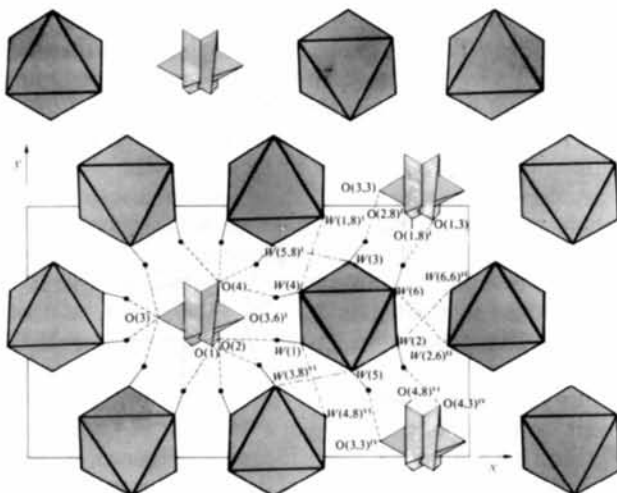


Fig. 1. Orthogonal projection onto the plane (001) of one layer of the structure of  $\beta$ - $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  emphasizing the close packing of  $\text{Na}(\text{H}_2\text{O})_6$  octahedra with sites occupied by  $\text{PO}_4$  tetrahedra disordered around the twofold axis. Ordered H atoms are shown as filled circles with the corresponding pair of alternative hydrogen bonds (dotted and dashed lines). Dashed-dotted lines represent other intra-layer hydrogen bonds; the inter-layer bonds are not reported.

the structure, and by the consequent disorder of P tetrahedra. The acidic H(7) atom is disordered over two positions related by the twofold axis. Each water molecule comprises an ordered H atom and another disordered over two independent positions; the molecule can be represented as distributed between two positions connected by rotation around its ordered O–H bond (BC, Table 4) by an angle of roughly 120°.

The configuration around each water molecule can be summarized as follows.

(i) A tetrahedral environment of class 2 type G (Ferraris & Franchini-Angela, 1972) is attained, by three hydrogen bridges and a coordination bond with Na.

(ii) In consequence of the disorder of the P tetrahedron, the hydrogen bond involving the ordered H atom of each water molecule is alternately donated to two different anionic O atoms (dashed and dotted lines in Fig. 1 respectively); the corresponding  $W\text{--}H\cdots\text{O}$  angles are then quite different from 180° and can be compared to those found in bifurcated hydrogen bonds. Very different distances are observed for the two alternative  $W\cdots\text{O}$  contacts, about 3.0 and 2.6 Å, respectively, in most cases. This kind of hydrogen bond always lies within the (001) layer.

(iii) The two remaining hydrogen bridges, one of which lies in the layer (dashed-dotted lines in Fig. 1) while the other links adjacent layers (not shown in Fig. 1), involve the disordered H atom of the water molecule; they interchange the donor/acceptor role according to the two configurations shown in Table 4. These two bridges are shared by the same water molecules in both configurations, except for  $W(1)$  which in the two configurations forms the inter-layer bond with two different anionic O atoms.

By considering the anionic O atoms, O(1), O(3) and O(4) are acceptors of three (one of which is inter-layer), four and four hydrogen bonds, respectively; on the other side, O(2) is an acceptor of two hydrogen bonds and a donor of one (out of the layer). This uneven distribution, presumably related to the requirements of close packing, causes some imbalance of bond strengths (Brown, 1976; Brown & Wu, 1976) for the underbonded O(1) and for the overbonded O(2) (1.83 and 2.18 v.u. respectively);\* this situation was even worse, of course, in the  $Cc$  model, where  $W(4)$  was caused to be quite underbonded by donating a very short hydrogen bond (2.457 Å).

#### The disorder

The least-squares refinement and crystallochemical results show that the  $C2/c$  disordered model is undoubtedly more realistic than the  $Cc$  ordered one.

\* The contribution from the hydrogen bonds has been calculated by the Lippincott & Schroeder curve given by Brown (1976).

Table 4. Bond lengths (Å) and angles ( $^\circ$ ) involving hydrogen bonds

For each water molecule two configurations are reported corresponding to the positions attained through rotation around BC. For the e.s.d.'s see Table 3 (H positions not refined).

A	B	C	D	E	AC	CE	AB	BC	CD	DE	ABC	CDE	BCD	ACE
O(2)...	H(1)–W(1)		H(8)···O(1,2) <sup>v</sup>		3.042	2.789	2.18	0.92	0.95	1.85	157	171	111	101.6
			H(11',8) <sup>vii</sup> –W(4,8) <sup>vii</sup>			2.821			2.00	0.85				
O(3,6) <sup>i</sup> ...	H(1)–W(1)		H(7,5) <sup>viii</sup> –O(2,5) <sup>viii</sup>		2.792	2.700	1.97	0.92	1.72	1.01	148	172	103	118.0
			H(8')···W(4,8) <sup>vi</sup>			2.821			0.92	1.91		162	110	103.8
O(4,3) <sup>iv</sup> ...	H(2)–W(2)		H(9)···W(4,2) <sup>v</sup>		3.034	2.786	2.23	0.86	0.95	1.87	156	166	112	121.6
			H(13',6) <sup>ii</sup> –W(6,6) <sup>ii</sup>			2.786			1.76	1.04		166	107	99.7
O(4,8) <sup>vi</sup> ...	H(2)–W(2)		H(11',2)–W(4,2) <sup>v</sup>		2.619	2.786	1.77	0.86	1.87	0.94	166	170	112	121.6
			H(9')···W(6,6) <sup>ii</sup>			2.786			0.87	1.93		166	107	99.7
O(3,3)...	H(3)–W(3)		H(10)···W(5,8) <sup>i</sup>		3.050	2.795	2.18	0.93	0.86	1.98	156	166	107	99.7
			H(10',7) <sup>viii</sup> –W(3,7) <sup>viii</sup>			2.780			1.95	0.86				
O(1,8) <sup>i</sup> ...	H(3)–W(3)		H(12',8) <sup>i</sup> –W(5,8) <sup>i</sup>		2.651	2.795	1.80	0.93	1.90	0.91	153	163	97	89.9
			H(10')···W(3,7) <sup>viii</sup>			2.780			0.83	1.95		164	110	101.0
O(4)...	H(4)–W(4)		H(11)···W(1,8) <sup>i</sup>		3.203	2.821	2.42	0.86	0.85	2.00	152	164	110	101.0
			H(9,2) <sup>iii</sup> –W(2,2) <sup>iii</sup>			2.786			1.87	0.95				
O(3,6) <sup>i</sup> ...	H(4)–W(4)		H(8',8) <sup>i</sup> –W(1,8) <sup>i</sup>		2.561	2.821	1.75	0.86	1.91	0.92	158	166	113	114.7
			H(11')···W(2,2) <sup>iii</sup>			2.786			0.94	1.87		166	105	113.3
O(3,3) <sup>iv</sup> ...	H(5)–W(5)		H(12)···W(6,5) <sup>viii</sup>		3.062	2.778	2.22	0.91	0.82	1.99	155	162	105	113.3
			H(10,8) <sup>vi</sup> –W(3,8) <sup>vi</sup>			2.795			1.98	0.83				
O(4,8) <sup>vi</sup> ...	H(5)–W(5)		H(13',5) <sup>viii</sup> –W(6,5) <sup>viii</sup>		2.620	2.778	1.76	0.91	1.94	0.85	157	168	114	129.1
			H(12')···W(3,8) <sup>vi</sup>			2.795			0.91	1.90		171	115	106.3
O(1,3)...	H(6)–W(6)		H(13)···W(2,6) <sup>ii</sup>		2.992	2.786	2.07	0.93	1.04	1.76	170	171	115	106.3
			H(12,5) <sup>viii</sup> –W(5,5) <sup>viii</sup>			2.778			1.99	0.82				
O(2,8) <sup>i</sup> ...	H(6)–W(6)		H(9',6) <sup>ii</sup> –W(2,6) <sup>ii</sup>		2.727	2.786	1.84	0.93	1.93	0.87	160	170	100	92.1
			H(13')···W(5,5) <sup>viii</sup>			2.778			0.85	1.94		164		
	O(2)–H(7)...		W(1,5) <sup>vii</sup>			2.700			1.01	1.72				

However, the question can be raised as to whether the disorder is dynamic or static.

Since the alternative configurations are related by a symmetry element belonging to the Laue symmetry of the configuration itself, except for the disordered H atoms of the water molecules, their contributions to each reflexion are the same on an absolute scale. As already described for twins by merohedry (Catti & Ferraris, 1976), if the different configurations do not contribute coherently to the scattering process, because they are confined to different domains of the mosaic, the best refinement is achieved for a model containing only one configuration. On the basis of the refinement results this situation does not apply here, so the two configurations are shown to contribute coherently to the scattering. This could be ascribed, in principle, to either dynamic or static disorder; however, some arguments seem to support a dynamically disordered model.

First, the disordered  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{O}$  groups in the structure are molecular units and the two disordered positions for each unit can be related by a simple rotation of the molecule itself around a definite direction. There are several cases of this kind in the literature, where the dynamic nature of the disorder has been proved by non-diffraction methods [cf. for example, potassium alum (Eysel & Schumacher, 1977)]; on the other side, static disorder generally

involves cases of atomic substitutions where the two configurations cannot be related by any movements of rigid groups (cf. the disorder caused by Al/Si diadochy in tectosilicates). Second, the closeness to the dehydration temperature means that atoms are located in shallow potential wells and, owing to their high thermal energy (the root-mean-square displacements in thermal ellipsoids of water molecules range from 0.18 to 0.27 Å), it is likely that low potential barriers between different orientations can be easily overcome.

According to the model of dynamic disorder, the whole structure would seem to be a large system of many penduli all jumping, in phase, between their two possible orientations through rotational motion of  $180^\circ$  around the twofold axis for the  $\text{HPO}_4^{2-}$  ion, and of about  $120^\circ$  around an O–H direction for the  $\text{H}_2\text{O}$  molecules. In the latter case, the axis of rotation is a centre-to-corner direction of the tetrahedral environment, so that the two lone-pair orbitals of  $\text{H}_2\text{O}$  point to Na and to the donor atom in one configuration, and switch to the ex-acceptor (now donor) atom and to Na, respectively, in the other configuration. The whole motion appears to be triggered by the pseudo-hexagonal symmetry of the  $\text{HPO}_4^{2-}$  site and propagated to the water molecules through the acidic hydrogen bond donated by O(2).

The larger environmental difference between the two configurations is represented by the remarkable

variations in length of the hydrogen bridges involving the ordered H atoms (*AC*, Table 4). On the basis of well known O—H *vs* O...O correlations, H(1),...,H(6) are, therefore, expected to move slightly along the corresponding *W*—H direction; in fact, this secondary type of disorder is witnessed by the thermal motion which is systematically larger for H(1),...,H(6) than for the other H atoms.

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### References

- BROWN, I. D. (1976). *Acta Cryst.* A32, 24–31.
- BROWN, I. D. & WU, K. K. (1976). *Acta Cryst.* B32, 1957–1959.
- CATTI, M. & FERRARIS, G. (1976). *Acta Cryst.* A32, 163–165.
- CATTI, M., FERRARIS, G. & FRANCHINI-ANGELA, M. (1977). *Acta Cryst.* B33, 3449–3452.
- EYSEL, H. H. & SCHUMACHER, G. (1977). *Chem. Phys. Lett.* 47, 168–170.
- FERRARIS, G. & FRANCHINI-ANGELA, M. (1972). *Acta Cryst.* B28, 3572–3583.
- GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- PASCAL, P. (1966). *Nouveau Traité de Chimie Minérale*. Vol. II. Paris: Masson.
- RAE, A. D. (1974). *Acta Cryst.* A30, 761–768.
- STEINMETZ, H. (1921). *Z. Kristallogr.* 56, 157–166.
- STEWART, J. M., KUNDALL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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## Neutron Diffraction Refinement of Paraelectric CsH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>

BY SAJEE CHOMNILPAN,\* ROLAND TELLGREN AND RUNE LIMINGA

*Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden*

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The crystal structure of the paraelectric phase of caesium trihydrogenselenite has been refined with a three-dimensional set of single-crystal neutron diffraction data. The crystals are triclinic, space group *P*1, with two formula units in a cell of dimensions:  $a = 9.3474$  (5),  $b = 6.5398$  (4),  $c = 5.8498$  (3) Å,  $\alpha = 91.443$  (6),  $\beta = 105.336$  (6), and  $\gamma = 91.629$  (6)°. A full-matrix least-squares refinement based on *F* gave a final *R* value of 0.032. The structure consists of H<sub>2</sub>SeO<sub>3</sub> molecules and HSeO<sub>3</sub><sup>-</sup> ions hydrogen-bonded together to form chains by means of four different hydrogen bonds all crossing centres of symmetry. This situation results in disordered half-occupied H positions. A fifth disordered hydrogen bond without symmetry restrictions interlinks the two types of chains to form a three-dimensional network. The refinement indicates that the occupancies of the two possible H sites in this bond are 0.68 and 0.32.

### Introduction

Caesium trihydrogenselenite undergoes a transition to an antiferroelectric phase at -128°C, as reported by Makita (1965). It is quite common, in the paraelectric phase of hydrogen-bonded ferro- or antiferroelectric crystals, for the H atoms to be disordered. A well-known example is the KDP family of ferroelectrics. In the paraelectric phase the H bonds often cross some

symmetry element such as an inversion centre, necessitating that the H atom be either located at the centre of symmetry or disordered in half-occupied positions. The latter assumption is normally the more reasonable, especially for hydrogen bonds longer than 2.5 Å. It was shown in a previous X-ray diffraction study of CsH<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub> (Tellgren & Liminga, 1974a) that four of the five hydrogen bonds cross centres of symmetry, with the H atoms disordered over the two sites of a double-minimum well. The remaining hydrogen bond has no symmetry restrictions imposed, however. The X-ray study indicated that this bond is

\* Permanent address: Department of Physics, Chulalongkorn University, Bangkok, Thailand.