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Single-crystal neutron diffraction study of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ ($x \simeq 0.5$) at 15 K

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Abstract

The structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ has been examined by single-crystal neutron diffraction at 15 K. The compound crystallizes in space group $C2/c$ and contains four formula units in the unit cell, with lattice parameters a = 19.769 (9), b = 7.685 (2), c = 8.858 (3) Å and β = 100.60 (4)°. Refinement of P, S and H site occupancies indicated that the value of x (in the stoichiometry) is 0.500 (6). This, together with the unit-cell volume of 1322.8 (14) Å^3, implies a density of 3.463 Mg m^{-3}. The structure contains zigzag rows of XO_4 anions, where X = P or S, that alternate, in a checkerboard fashion, with zigzag rows of Cs cations. Moreover, there is one proton site, H(3), with an occupancy of 0.25 and one X-atom site, X(1), that is occupied by 0.5 P and 0.5 S. These features are in general agreement with a previous X-ray structure determination carried out at 298 K. In contrast to the X-ray study, however, it was found that two different structural models adequately fit the diffraction data. In the first model, the proton vacancies and the P atoms were assumed to be randomly distributed over the H(3) and X(1) sites, respectively, and to have no impact on the local structure. In the second model, several atoms were assigned split occupancies over two neighboring sites, to reflect the presence or absence of a proton vacancy, and the presence of P or S on the X(1) site. Refinement assuming the first model, in which anisotropic displacement parameters for 12 of 14 atom sites in the asymmetric unit were employed, yielded residuals $wR(F^2)$ = 0.084 and $wR(F)$ = 0.038. For the second model, in which anisotropic displacement parameters were utilized for only the five atoms that were not split relative to the first model, the residuals were $wR(F^2)$ = 0.081 and $wR(F)$ = 0.036.

1. Introduction

Several solid acid sulfates and selenates, such as $CsHSO_4$ (Baranov *et al.*, 1982) and $Rb_3H(SeO_4)_3$ (Pawlowski *et al.*, 1990), have been the subject of structural and electrical characterization studies because they undergo superprotonic phase transitions at slightly elevated temperatures. The compound $CsHSO_4$, for example, exhibits an increase in conductivity by almost four orders of magnitude upon undergoing a transition at 414 K (Baranov *et al.*, 1982). Recently, we reported the X-ray structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ (Haile *et al.*, 1998), a new mixed sulfate–phosphate that also undergoes a structural transition to a phase of high conductivity upon heating (Haile *et al.*, 1997).

The X-ray structure determination of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ (Haile *et al.*, 1998) revealed that it is composed of alternating zigzag rows of XO_4 groups (where X = P or S) and of Cs ions, in a manner very similar to that observed for $CsHSO_4$-II (Belushkin *et al.*, 1991). The XO_4 rows contain two crystallographically distinct XO_4 groups, with the first, $X(1)O_4$, residing at a 4e site, and the second, $X(2)O_4$, residing at an 8f site. While the distribution of P and S on the two X-atom sites and the location of protons could not be determined directly from the X-ray data, the measured composition of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ and the structural similarity between β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ and α-$Cs_3(HSO_4)_2[H_2PO_4]$ (Haile, Kreuer & Maier, 1995) suggested that the X(1) site was occupied by 0.5 S and 0.5 P and that the X(2) site was completely occupied by S. Moreover, the distances between O atoms of neighboring XO_4 groups indicated that there were two hydrogen bonds of typical lengths [2.474 (9) and 2.597 (8) Å], and possibly a third, very long [3.163 (10) Å] hydrogen bond in the structure. The stoichiometry of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ further suggested that the first two bonds, those between O(1) and O(1′) and between O(2) and O(3), corresponded to fully occupied proton sites, and the third, between O(5) and O(6), to a partially occupied site. The objective of the present neutron study was thus to determine directly the P and S distribution over the X-ion sites, and to locate directly the protons in the structure. The latter point is particularly relevant to understanding the mechanism of proton transport in this compound.

2. Experimental

The growth and chemical analysis of crystals of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ have been described elsewhere. Briefly, colorless crystals were obtained from aqueous solution by slow evaporation over a period of five to seven days; analytical chemical methods showed these crystals to have an overall stoichiometry of approximately $Cs_3(HSO_4)_{2.5}(H_2PO_4)_{0.5}$ (Haile *et al.*, 1998).

Diffraction data were obtained on the four-circle diffractometer at beam port H6M of the High Flux Beam Reactor at Brookhaven National Laboratory. The neutron beam, monochromated by beryllium (002) planes in reflection geometry, had a wavelength of 1.0462 (1) Å as calibrated against KBr, a_o = 6.6000 Å at 298 K. The sample was sealed in an aluminium container under a helium atmosphere, and placed in a DISPLEX Model CS-202 closed-cycle refrigerator (APD Cryogenics, Inc.). Following a preliminary examination at 240 K, the crystal was cooled to 15.0 (5) K, at which temperature the crystal was maintained throughout the measurements. The temperature was monitored with a platinum resistance thermometer. The space group determined at room temperature from the X-ray data was *C*2/*c*. Because it was not known whether the material underwent any phase transitions upon cooling, a careful check of systematic absences was performed. The lattice remained *C*-centered and the data were collected assuming the nonprimitive cell. Full details of the crystal data and data collection procedure are provided in Table 1.

Table 1. *Crystal data, data collection parameters and other experimental details for the collection of neutron diffraction data for* β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

Temperature	15.0 (5) K
Formula	$Cs_3S_{2+x}P_{1-x}O_{12}H_{4-x}$, $x \simeq 0.5$
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit-cell dimensions	*a* = 19.769 (9) Å *b* = 7.685 (2) Å *c* = 8.858 (3) Å β = 100.60 (4)°
Unit-cell volume	1322.8 (14) Å^3
Formula weight	689.9
Z	4
Density (calculated)	3.463 Mg m^{-3}
Absorption coefficient	5.96 mm^{-1}
Crystal size	1.4 × 3.2 × 2.2 mm
Crystal shape	Plate-like
Crystal habit (forms)	±(100) ±(010) ±(001)
Crystal color	Colorless
Crystal mount	Aluminium pin with halocarbon grease
Number of reflections for cell measurement	3240
2θ range for cell measurement	40–59°
Radiation	Neutron
Instrument	H6M port, High Flux Beam Reactor, Brookhaven National Laboratory
Wavelength	1.0462 (1) Å
Monochromator	Be (002)
Data collection method	ω–2θ scan (McMullan *et al.*, 1979)
F(000)	327.0304 fm
Absorption correction method	Analytical
Maximum and minimum transmission factors	0.925 and 0.870
2θ range for data collection	6–108°
Index ranges	$0 \le h \le 30$ $0 \le k \le 11$ $-13 \le l \le 13$
Number of reflections collected	2858 (assuming *C*-centering)
Number of independent reflections	2570 [$R_{\rm int}(F^2)$ = 0.0349]
Number of significant reflections	1475 [$I > 3\sigma(I)$]
Standards	$\bar{4}\bar{4}\bar{4}$, $40\bar{8}$
Deviation of standards from inital value	Stable
Decay correction	None applied

3. Refinement: two structural models of β-$Cs_3(HSO_4)_2$-$[H_{2-x}(S_xP_{1-x})O_4]$

The neutron structure of β-$Cs_3(HSO_4)_2$-$[H_{2-x}(S_xP_{1-x})O_4]$ was refined using, as initial values, the coordinates determined from the X-ray diffraction study (Haile *et al.*, 1998). The first task in the neutron refinement was to locate the protons in the structure. To this end, a difference Fourier map was constructed using the Cs, P, S and O atoms. In agreement with the conclusions drawn on the basis of O···O distances, three proton sites were identified, the first residing at a special position and linking O(1) and O(1′), the second linking O(2) and O(3), and the third weakly linking O(5) and O(6).

In order to determine the distribution of P and S on the two *X*-ion sites and that of the protons on the three H-atom sites, and thereby establish the stoichiometry of the compound, the occupancies at these sites were refined with P placed at the *X*(1) site and S at the *X*(2) site. With the exception of *X*(1) and H(3), all occupancies refined to values within 3 standard uncertainties (s.u.'s) of 1. The occupancy factor at the *X*(1) site, 0.778 (10) by P, corresponds to that expected for full occupancy by 0.5 P and 0.5 S, which have scattering lengths of 5.13 and 2.847 fm, respectively (Sears, 1993), and is in agreement with the chemical analysis. From here on the scattering length for the *X*(1) position was set at 3.9885 fm, the average of the scattering lengths for P and S, and the occupancy fixed at 1. The occupancy at the H(3) site took on a value of 0.26 (1), which is also in agreement with the chemical analysis: an occupancy of 0.25 at this site together with full proton occupancies at the two other hydrogen bonds implies an overall proton content of 3.5 H per formula unit. In subsequent analyses the occupancy was thus fixed at 0.25. The occupancies at both sites were periodically checked at later stages of the structure refinement, and in all cases the values assigned here were obtained, within 1 or 2 s.u.'s.

The next question to be resolved was the exact location of H(1) relative to the special position at 0, 0, 1/2. The O(1)···O(1′) distance was ~2.45 Å, a value just at

Table 2. *Final refinement parameters for* β*-*$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

	Model 1	Model 2
Refinement method	F^2	F^2
$R(F^2)$	0.111	0.108
$wR(F^2)$	0.084	0.081
$R[F_o > 3\sigma(F_o)$, 1475 reflections]	0.054	0.052
$wR(F)$	0.038	0.036
Goodness of fit, S, on F^2	1.30	1.25
Number of relections used in refinement	2568	2568
Number of refined parameters	104	97
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max}$	< 0.1	< 0.1
Maximum/minimum difference Fourier peaks	4.5%/3.0% of Cs(2)	3.7%/3.4% of Cs(2)
Anisotropic displacement parameters	Applied to most atoms (Table 3)	Applied to selected atoms (Table 4)
Extinction method	None applied	None applied
Source of scattering lengths	Sears (1993)	Sears (1993)
Structure solution	X-ray solution	X-ray solution
Structure refinement	*UPALS* (Lundgren, 1982)	*UPALS* (Lundgren, 1982)
Molecular graphics	*ATOMS* (Dowty, 1997)	*ATOMS* (Dowty, 1997)

the limit between single-minimum and double-minima hydrogen bonds (Ichikawa, 1978). A difference Fourier map constructed excluding H(1) exhibited a rather broad peak between the two O(1) atoms, and thus refinements with H(1) both slightly displaced from and directly on the symmetry position were pursued. The residual was only slightly lower for the former case, despite the significantly greater number of parameters. In addition, the displacement ellipsoid of the disordered H(1) had an unsatisfying disc-like shape (with the short axis parallel to the O···O bond), whereas that of the ordered H(1) was a more realistic elongated ellipsoid (with the long axis parallel to the O···O bond). Therefore, H(1) was fixed at the symmetry position for the remainder of the refinement. It was then noted that the H(2) atom exhibited unusually large displacements, particularly in a direction along the O(2)—O(3) bond. Moreover, difference Fourier maps, constructed from Fourier syntheses in which the proton was omitted, showed two peaks between O(2) and O(3) with an intensity ratio of approximately 3:1. Therefore, a somewhat unusual split-atom model for the H(2) proton was adopted, with one site closer to O(3), designated H(21), and the other closer to O(2), designated H(22). For subsequent refinements, the sum of the occupancies at these two sites was constrained to 1, and the isotropic displacement factors of these two species were constrained to be equal.

In the final refinement, the occupancy factors of all atoms, with the exception of H(21) and H(22), were fixed and all atoms, with the exception again of H(21) and H(22), were treated anisotropically. The structure was refined using 2568 independent F_o^2 values; calculations were carried out with the *UPALS* program (Lundgren, 1982). The scale factor was varied, together with positional and displacement parameters for the 14 atoms comprising the asymmetric unit. No extinction correction was included, since a refinement [using an isotropic model of type I with Lorentzian mosaicity after Becker & Coppens (1974)] did not result in a significant value for the extinction coefficient. A total of 104 variables were refined until convergence was achieved, according to the criterion $\Delta/\sigma < 0.1$. Final agreement factors for this model are as follows: $R(F^2) = 0.111$, $wR(F^2) = 0.084$, $S = 1.30$, with weights $w = 1/\sigma^2(F)$, and the conventional $wR(F) = 0.038$ for 1475 reflections with $F_o > 3\sigma(F_o)$. Further details of the refinement are given in Table 2, along with the results of an alternative refinement, discussed below. Atomic coordinates and displacement parameters obtained from this first model, which from here on will be referred to as Model 1 or the simple model, are presented in Table 3.

While this model adequately fits the diffraction data, several of the displacement parameters were unsatisfactorily large [particularly those of O(5), O(6) and Cs(2); Table 3]. Furthermore, the O(6)—H(3) distance of 1.301 (8) Å was much longer than a typical O—H bond, and the S(2)—O(6)—H(3) angle of 97.3 (3)° was unusually sharp. These observations led us to suspect that the structure crystallized in a space group of lower symmetry, if not in terms of the long-range structure, then perhaps in terms of the short-range structure. Moreover, a few systematic-absence violations of the *C*-centering had been observed in the X-ray data collection (specifically, five of approximately 1430 peaks with indices $h + l = 2n + 1$ had intensity greater than 4σ), suggesting that the crystal structure might be better described by a primitive unit cell. Therefore, several alternative structural models were examined, including refinements in the lower-symmetry space groups $P2/c$, $P2$, Pc (noncentered) and Cc (noncentrosymmetric). In all cases, pseudosymmetry-related atoms were generated and refinement was carried out by either letting all parameters vary independently, or by explicitly linking the values of selected parameters. Where the refinement did not simply fail, all pseudosymmetry-related para-

Table 3. *Atomic coordinates and displacement parameters of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ according to Model 1*

	Site	x	y	z	U^{11}/U_{eq}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs(1)	4*e*	1/2	0.4015 (2)	1/4	0.0088 (7)	0.0076 (7)	0.0112 (7)	0	−0.0006 (5)	0
Cs(2)	8*f*	0.3228 (1)	0.1375 (2)	0.3817 (2)	0.0065 (5)	0.0110 (5)	0.0399 (8)	0.0011 (4)	−0.0009 (5)	−0.0083 (5)
P/S(1)	4*e*	1/2	0.9050 (3)	1/4	0.0114 (9)	0.0053 (8)	0.0030 (7)	0	0.0004 (7)	0
O(1)	8*f*	0.5266 (1)	0.0191 (1)	0.1356 (1)	0.0121 (4)	0.0095 (4)	0.0084 (4)	−0.0029 (4)	0.0006 (3)	−0.0010 (4)
O(2)	8*f*	0.4423 (1)	0.7946 (2)	0.1675 (1)	0.0186 (5)	0.0095 (5)	0.0095 (4)	−0.0052 (4)	0.0002 (4)	−0.0009 (4)
S(2)	8*f*	0.1584 (1)	0.1319 (3)	0.0692 (3)	0.0087 (8)	0.0089 (9)	0.0137 (9)	0.0035 (8)	0.0018 (7)	−0.0004 (8)
O(3)	8*f*	0.1666 (1)	0.7651 (2)	0.7203 (1)	0.0121 (5)	0.0138 (5)	0.0076 (4)	−0.0034 (4)	−0.0009 (3)	0.0024 (4)
O(4)	8*f*	0.1014 (1)	0.9845 (2)	0.5606 (1)	0.0276 (6)	0.0265 (7)	0.0129 (5)	0.0127 (6)	0.0021 (5)	0.0042 (5)
O(5)	8*f*	0.2226 (1)	0.9574 (2)	0.5732 (2)	0.0193 (6)	0.0416 (9)	0.0320 (7)	−0.0198 (6)	−0.0073 (5)	0.0221 (7)
O(6)	8*f*	0.1449 (1)	0.7405 (2)	0.4441 (1)	0.0505 (9)	0.0130 (5)	0.0095 (4)	0.0073 (6)	0.0003 (5)	−0.0022 (4)
H(1)	4*b*	1/2	0	0	0.0308 (16)	0.0223 (15)	0.0418 (17)	0	0.0167 (14)	0
H(21)†	8*f*	0.1199 (2)	0.7476 (5)	0.7557 (4)	0.0246 (6)					
H(22)‡	8*f*	0.0949 (5)	0.7246 (11)	0.7829 (9)	0.0246 (6)					
H(3)	8*f*	0.2080 (4)	0.6885 (11)	0.4516 (8)	0.022 (4)	0.017 (3)	0.015 (3)	−0.002 (3)	0.005 (3)	0.005 (3)

† Refined occupancy of 0.698 (7). ‡ Refined occupancy of 0.302 (7).

meters (that were not explicitly linked) were correlated above the 80% level. Furthermore, in no case did the magnitudes of the s.u.'s of refined parameters or chemical reasonableness of the solution improve. Hence, $C2/c$ was taken as the correct space group and alternative models within the constraints of this space group examined.

Eventually, the most satisfactory model identified was one in which those atoms with large displacement parameters (in Model 1) were split so as to partially occupy two closely neighboring sites, *e.g.* O(5) was split into two atoms O(51) and O(52), each with occupancy 0.5. Initially, only the atoms O(4), O(5) and O(6) [in addition to the already split H(2) atom] were refined in such a manner; however, physically more satisfactory coordination polyhedra were obtained with all atoms except P/S(1), Cs(1) and O(1) refined as split atoms. Because of the proximity of atomic sites within a pair, the displacement parameters were highly correlated and thus all atoms in such sites were constrained to have isotropic displacement parameters. At this stage, simultaneous refinement of the occupancy factors of the 18 independent non-Cs atoms in the asymmetric unit and of all displacement parameters yielded, for the most part, occupancies at split atom sites that were within 3 s.u.'s of 0.5. The exceptions [in addition to the H(21)/H(22) pair] were the S(21)/S(22) pair, for which occupancies could not be simultaneously refined because of extremely large correlations, and the O(61)/O(62) pair, for which higher occupancy on the O(61) site was preferred. While a slightly improved residual could be attained by allowing the occupancies of the O(61)/O(62) pair to take on their refined values, it was deemed physically unreasonable for these occupancies to differ from those of other members of the SO_4 group, and thus all occupancies of split atoms were subsequently fixed at 0.5. Upon finalizing the details of this model, which from here on will be referred to as Model 2 or the complex model, a check of the position of the H(1) atom relative to the symmetry position at 0, 0, 1/2 was conducted. A difference Fourier map was again constructed excluding the H(1) atom, and again, a single broad peak between the O(1) atoms was observed. In this case, refinement with the proton directly on the center of symmetry yielded a slightly lower residual than a refinement with the proton slightly displaced, and H(1) was accordingly kept fixed at the symmetry position.

The final refinement of Model 2 was carried out in the same manner as that of Model 1 with the following exceptions: 21 atoms comprised the asymmetric unit, occupancies at all atom sites were fixed as given in Table 4, and anisotropic displacement parameters were utilized only for those atoms which were not split relative to Model 1, giving rise to a total of 97 variables. Final agreement factors were as follows: $R(F^2) = 0.108$, $wR(F^2) = 0.081$, $S = 1.25$, and $wR(F) = 0.052$. Full details of the refinement are provided in Table 2, and atomic coordinates and displacement parameters are listed in Table 4.

4. Results

Cation coordination polyhedra obtained by the simple and complex models are compared in Tables 5 and 6. The sums of the bond valences at each of the cations are also provided in these tables, where the valences of the Cs—O, P—O and S—O bonds were determined according to

$$S(\mathrm{Cs-O}) = \exp[(2.417 - d_{\mathrm{Cs-O}})/0.37], \qquad (1)$$

$$S(\mathrm{P-O}) = \exp[(1.617 - d_{\mathrm{P-O}})/0.37] \qquad (2)$$

and

$$S(\mathrm{S-O}) = \exp[(1.624 - d_{\mathrm{S-O}})/0.37] \qquad (3)$$

(Brown & Altermatt, 1985), where $d_{\mathrm{Cs-O}}$, $d_{\mathrm{P-O}}$ and $d_{\mathrm{S-O}}$ are the respective bond distances, measured in Å. In Table 7 a comparison of the hydrogen-bond geome-

Table 4. *Atomic coordinates and displacement parameters of* β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ *according to Model 2*

	Site	x	y	z	Occupancy
Cs(1)	4*e*	1/2	0.4013 (2)	1/4	1
Cs(21)	8*f*	0.3221 (1)	0.1326 (4)	0.4006 (3)	0.5
Cs(22)	8*f*	0.3233 (1)	0.1423 (3)	0.3645 (3)	0.5
P/S(1)	4*e*	1/2	0.9051 (3)	1/4	1
O(1)	8*f*	0.5266 (1)	0.0192 (1)	0.1357 (1)	1
O(21)	8*f*	0.4471 (2)	0.7894 (5)	0.1661 (4)	0.5
O(22)	8*f*	0.4373 (2)	0.7999 (5)	0.1690 (4)	0.5
S(21)	8*f*	0.1585 (5)	0.1328 (14)	0.0628 (11)	0.5
O(31)	8*f*	0.1692 (2)	0.7559 (5)	0.7167 (4)	0.5
O(41)	8*f*	0.1069 (2)	0.9976 (4)	0.5618 (3)	0.5
O(51)	8*f*	0.2264 (1)	0.9388 (4)	0.5604 (3)	0.5
O(61)	8*f*	0.1375 (1)	0.7368 (3)	0.4449 (2)	0.5
S(22)	8*f*	0.1583 (6)	0.1306 (16)	0.0767 (12)	0.5
O(32)	8*f*	0.1640 (2)	0.7747 (5)	0.7238 (4)	0.5
O(42)	8*f*	0.0956 (2)	0.9707 (4)	0.5591 (3)	0.5
O(52)	8*f*	0.2185 (1)	0.9773 (4)	0.5867 (3)	0.5
O(62)	8*f*	0.1560 (2)	0.7459 (4)	0.4432 (3)	0.5
H(1)	4*b*	1/2	0	0	1
H(21)	8*f*	0.1195 (2)	0.7474 (4)	0.7560 (3)	0.75
H(22)	8*f*	0.0936 (5)	0.7230 (11)	0.7833 (9)	0.25
H(3)	8*f*	0.2080 (4)	0.6882 (11)	0.4505 (8)	0.25

	U^{11}/U_{eq}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs(1)	0.0081 (7)	0.0074 (6)	0.0114 (6)	0	−0.0009 (5)	0
Cs(21)	0.0093 (6)					
Cs(22)	0.0070 (5)					
P/S(1)	0.0113 (9)	0.0048 (8)	0.0024 (7)	0	0.0001 (7)	0
O(1)	0.0117 (4)	0.0097 (4)	0.0080 (4)	−0.0028 (4)	0.0004 (3)	−0.0010 (3)
O(21)	0.0078 (8)					
O(22)	0.0092 (9)					
S(21)	0.006 (3)					
O(31)	0.0070 (9)					
O(41)	0.0129 (6)					
O(51)	0.0121 (5)					
O(61)	0.0040 (4)					
S(22)	0.012 (3)					
O(32)	0.0085 (9)					
O(42)	0.0144 (7)					
O(52)	0.0130 (5)					
O(62)	0.0189 (6)					
H(1)	0.028 (2)	0.021 (2)	0.043 (2)	0	0.015 (1)	0
H(21)	0.0266 (6)					
H(22)	0.0180 (14)					
H(3)	0.022 (4)	0.018 (3)	0.014 (3)	0.004 (3)	0.003 (3)	−0.002 (3)

tries obtained by the simple and complex models is provided, and in Table 8 the sums of the bond valences at the O anions both including and excluding protons are listed. In this case, the valence of an O—H bond was calculated using the parameters of Alig *et al.* (1994),

$$S(\mathrm{O{-}H}) = \exp[(0.914 - d_{\mathrm{O-H}})/0.404], \qquad (4)$$

where $d_{\mathrm{O-H}}$ is the bond distance, again, measured in Å. In Tables 6–8 donor and acceptor O atoms are denoted by the subscripts D and A, respectively, where the hydrogen-bond configuration is given by $X{-}O_D{-}H\cdots O_A{-}X$; mixed donor/acceptor atoms result when the two O atoms are related by a center of symmetry or other symmetry operation, and such species are indicated by the subscript A/D.

5. Discussion

5.1. *General*

Projections on (101) and on (010) of the structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ according to Model 1 are presented in Figs. 1 and 2, respectively. The XO_4 rows that extend along $[10\bar{1}]$ are evident. These rows are linked to one another at the P/S(1)O_4 tetrahedral group *via* the O(1)–H(1)–O(1′) bond. Hydrogen bonding in the direction along which the XO_4 row extends occurs at two locations, first between the P/S(1)O_4 group and the S(2)O_4 group *via* the O(2)–H(22)/H(21)–O(3) bond, and second, between neighboring S(2)O_4 groups (Fig. 2). The linkage between S(2)O_4 groups is somewhat unusual in that there is a pair of ‘weak’ hydrogen bonds,

Table 5. *Interatomic distances (Å) and the sums of the bond valences in the caesium coordination polyhedra of* β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

See text (§4) for formula used to calculate the valence contribution from each Cs—O bond.

Model 1		Model 2			
Cs(1)—O(4)	2.972 (2)	Cs(1)—O(41)	3.023 (3)	Cs(1′)—O(42)	2.928 (4)
O(4)	2.972 (2)	O(41)	3.023 (3)	O(42)	2.928 (4)
O(4)	3.156 (1)	O(41)	3.239 (3)	O(42)	3.074 (3)
O(4)	3.156 (1)	O(41)	3.239 (3)	O(42)	3.074 (3)
O(1)	3.183 (2)	O(1)	3.182 (2)	O(1)	3.182 (2)
O(1)	3.183 (2)	O(1)	3.182 (2)	O(1)	3.182 (2)
O(2)	3.264 (2)	O(21)	3.202 (4)	O(22)	3.333 (4)
O(2)	3.264 (2)	O(21)	3.202 (4)	O(22)	3.333 (4)
O(6)	3.298 (2)	O(61)	3.200 (2)	O(62)	3.453 (3)
O(6)	3.298 (2)	O(61)	3.200 (2)	O(62)	3.453 (3)
ΣS = 1.36	Average = 3.18	ΣS = 1.34	Average = 3.17	ΣS = 1.38	Average = 3.19
Cs(2)—O(1)	3.144 (2)	Cs(22)—O(1)	3.115 (3)	Cs(21)—O(1)	3.187 (3)
O(5)	3.152 (2)	O(52)	3.052 (4)	O(51)	2.965 (4)
O(5)	3.155 (2)	O(51)	3.466 (4)	O(52)	3.111 (4)
O(2)	3.172 (2)	O(21)	3.317 (4)	O(22)	3.019 (4)
O(6)	3.170 (2)	O(61)	3.070 (4)	O(62)	3.216 (4)
O(3)	3.241 (2)	O(31)	3.153 (5)	O(32)	3.346 (5)
O(4)	3.266 (2)	O(41)	3.108 (4)	O(42)	3.443 (4)
O(5)	3.284 (2)	O(52)	3.352 (4)	O(51)	3.296 (4)
O(3)	3.242 (2)	O(32)	3.230 (4)	O(32)	3.464 (5)
O(6)	3.297 (2)	O(61)	3.385 (3)	O(62)	3.272 (4)
[O(3)]†	[3.627]†	[O(31)]†	[3.787]†	O(31)	3.273 (4)
ΣS = 1.22	Average = 3.21	ΣS = 1.23	Average = 3.22	ΣS = 1.31	Average = 3.24

† Not included in the calculation of $\langle d_{Cs-O} \rangle$, but included in ΣS.

O(5)–H(3)–O(6′) and O(6)–H(3′)–O(5′), and the proton site at H(3) has an occupancy of only 0.25, as discussed earlier. If one presumes that no two neighboring H(3) sites [which are separated by a distance of 1.97 (2) Å] linking O(5)–O(6) and O(5′)–O(6′) are simultaneously occupied, the overall 0.25 occupancy implies that half of all the SO_4–SO_4 neighbors along the chain are hydrogen bonded.

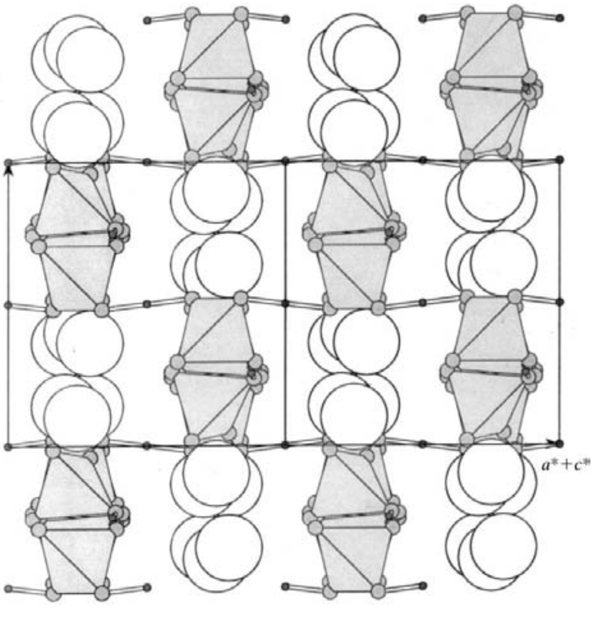

Fig. 1. The structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, Model 1, projected along [10$\bar{1}$]. Zigzag rows of XO_4 groups and of Cs cations extend out of the plane of the paper. Hydrogen bonds between XO_4 rows are shown. Hydrogen bonds along the length of the rows are not visible in this projection.

As noted above, a disturbing feature of this otherwise satisfactory model was the magnitude of certain displacement parameters. This is evidenced in Fig. 3, a displacement-ellipsoid representation of the structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, according to Model 1, projected along (010). The offending atoms are O(5) and O(6), those participating in the long hydrogen bond, and Cs(2). Such large displacement parameters can result if the unit cell or space group has been incorrectly identified, with large displacements masking the fact that pairs of atoms are not symmetry related. As indicated above, however, no evidence for a lower-symmetry space group was found. Thus, short-range rather than long-range ordering was deemed potentially responsible for these large displacements, particularly because any long-range ordering of P and S, which have very different neutron scattering lengths (5.13 and 2.847 fm, respectively), would be readily detectable by neutron diffraction.

The structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ according to Model 2 can be most easily understood as a superposition of two orientations of a structure with space group *P*2/*c*. Projections of this ‘local’ structure, in

Table 6. *Interatomic distances (Å), angles (°) and the sums of the bond valences in the sulfur and phosphorus coordination polyhedra in* $\beta\text{-}Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

See text (§4) for formula used to calculate the valence contribution from each X—O bond. Distances (Å) between neighboring sites in Model 2: Cs(21)–Cs(22) = 0.333 (4); O(21)–O(22) = 0.216 (5); S(21)–S(22) = 0.124 (15); O(31)–O(32) = 0.195 (5); O(41)–O(42) = 0.302 (5); O(51)–O(52) = 0.424 (4); O(61)–O(62) = 0.375 (4).

Model 1

P,S(1)—	Distance	Angle		
O(2)$_A$	1.500 (2)			
O(2′)$_A$	1.500 (2)	111.1 (2)		
O(1)$_{A/D}$	1.506 (2)	109.3 (1)	109.2 (1)	
O(1′)$_{A/D}$	1.506 (2)	109.2 (1)	109.3 (1)	108.8 (2)
		O(2)	O(2′)	O(1)
$\langle d_{\mathrm{P,S-O}}\rangle$	1.503			
ΣS	5.49			

O···O	Distance			
	O(2)	2.474 (2)		
	O(1)	2.450 (2)	2.452 (2)	
	O(1′)	2.452 (2)	2.450 (2)	2.449 (2)
		O(2)	O(2′)	O(1)

S(2)—	Distance	Angle		
O(5)$_{A^*}$	1.436 (3)			
O(4)	1.431 (3)	112.8 (2)		
O(6)$_{D^*}$	1.467 (3)	112.0 (2)	110.1 (2)	
O(3)$_D$	1.537 (3)	105.9 (2)	108.9 (2)	106.8 (1)
		O(5)	O(4)	O(6)
$\langle d_{\mathrm{S-O}}\rangle$	1.468			
ΣS	6.14			

O···O	Distance			
	O(4)	2.387 (2)		
	O(6)	2.407 (2)	2.376 (2)	
	O(3)	2.374 (2)	2.416 (2)	2.412 (2)
		O(5)	O(4)	O(6)

Model 2

P—	Distance	Angle		
O(22)$_{A/D}$	1.542 (4)			
O(22′)$_{A/D}$	1.542 (4)	116.7 (3)		
O(1)$_{A/D}$	1.506 (2)	110.1 (1)	105.5 (1)	
O(1′)$_{A/D}$	1.506 (2)	105.5 (1)	110.0 (1)	108.8 (1)
		O(22)	O(22′)	O(1)
$\langle d_{\mathrm{P-O}}\rangle$	1.524			
ΣS	5.15			

O···O	Distance			
	O(22)	2.626 (7)		
	O(1)	2.500 (4)	2.426 (4)	
	O(1′)	2.426 (4)	2.500 (4)	2.448 (2)
		O(22)	O(22′)	O(1)

S(1)—	Distance	Angle		
O(21)$_A$	1.466 (4)			
O(21′)$_A$	1.466 (4)	105.3 (3)		
O(1)$_{A/D}$	1.506 (2)	108.5 (1)	112.9 (1)	
O(1′)$_{A/D}$	1.506 (2)	112.9 (1)	108.5 (1)	108.8 (1)
		O(21)	O(21′)	O(1)
$\langle d_{\mathrm{S-O}}\rangle$	1.486			
ΣS	5.82			

O···O	Distance			
	O(21)	2.332 (6)		
	O(1)	2.412 (4)	2.477 (4)	
	O(1)	2.477 (4)	2.412 (4)	2.448 (2)
		O(21)	O(21)	O(1)

S(21)—	Distance	Angle		
O(51)$_A$	1.456 (11)			
O(41)	1.429 (11)	113.2 (7)		
O(61)	1.452 (10)	113.1 (7)	111.7 (6)	
O(31)$_D$	1.590 (11)	103.7 (6)	111.4 (7)	102.7 (7)
		O(51)	O(41)	O(61)
$\langle d_{\mathrm{S-O}}\rangle$	1.482			
ΣS	5.96			

O···O	Distance			
	O(41)	2.409 (4)		
	O(61)	2.426 (3)	2.385 (4)	
	O(31)	2.397 (5)	2.497 (5)	2.378 (4)
		O(51)	O(41)	O(61)

S(22)—	Distance	Angle		
O(52)	1.438 (12)			
O(42)	1.449 (12)	112.2 (8)		
O(62)$_D$	1.510 (12)	108.5 (8)	110.5 (7)	
O(32)$_{A/D}$	1.479 (12)	107.6 (7)	106.4 (8)	111.6 (8)
		O(52)	O(42)	O(62)
$\langle d_{\mathrm{S-O}}\rangle$	1.469			
ΣS	6.10			

O···O	Distance			
	O(42)	2.397 (4)		
	O(62)	2.393 (4)	2.431 (5)	
	O(32)	2.354 (5)	2.345 (5)	2.471 (5)
		O(52)	O(42)	O(62)

Table 7. *Hydrogen-bond geometry in* β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

Model	Bond	$X-O_D-H\cdots O_A-X$/ $X-O_A\cdots H-O_D-X$	$d(O\cdots O)$ (Å)	$d(O-H)$ (Å)	$d(O\cdots H)$ (Å)	$\angle O-H\cdots O$ (°)	$\angle X-O-H$ (°)	$H\cdots H$† (Å)	ΣS
X-ray	H(1)	$P/S(1)-O(1)_{A/D}\cdots H(1)\cdots O(1')_{A/D}-P/S(1')$	2.474 (9)	1.237‡	[1.237]‡	[180]‡	117.2‡	0‡	—
Model 1		$P/S(1)-O(1)_{A/D}\cdots H(1)\cdots O(1')_{A/D}-P/S(1')$	2.456 (2)	1.228 (1)	[1.228 (1)]	180	116.6 (1)	0	0.92
Model 2		$P-O(1)_{A/D}\cdots H(1)\cdots O(1')_{A/D}-P'$	2.458 (2)	1.229 (1)	[1.229 (1)]	180	116.6 (1)	0	0.92
X-ray	H(2)	$P/S(1)-O(2)_A\cdots H(2)-O(3)_D-S(2)$	2.597 (8)	n/a	n/a	n/a	n/a	n/a	
Model 1	H(2)	$P/S(1)-O(2)_A\cdots H(21)_{0.7}-O(3)_D-S(2)$	2.572 (2)	1 .037 (4)	1.544 (4)	170.2 (3)	111.9 (2)	0.615 (11)	0.66
		$P/S(1)-O(2)_A-H(22)_{0.3}\cdots O(3)_D-S(2)$	2.572 (2)	0.934 (10)	1.645 (10)	171.7 (7)	117.0 (5)	0.615 (11)	0.34
Model 2	H(2*a*)	$S(1)-O(21)_A\cdots H(21)-O(31)_D-S(21)$	2.715 (5)	1.104 (5)	1.620 (5)	170.3 (3)	108.4 (5)	0	0.80
	H(2*b*)	$P-O(22)_{A/D}\cdots H(21)_{1/2}-O(32)_{A/D}-S(22)$	2.437 (6)	0.996 (5)	1.452 (5)	169.1 (4)	115.8 (5)	0.634 (10)	0.54
		$P-O(22)_{A/D}-H(22)_{1/2}\cdots O(32)_{A/D}-S(22)$	2.437 (6)	0.822 (10)	1.626 (10)	168.3 (8)	118.9 (6)	0.634 (10)	0.71
X-ray	H(3)	$S(2)-O(6)_D-H(3)_{1/4}\cdots O(5)_A-S(2)$	3.163 (10)	n/a	n/a	n/a	n/a		
Model 1		$S(2)-O(6)_D-H(3)_{1/4}\cdots O(5)_A-S(2)$	3.058 (2)	1.300 (8)	1.818 (9)	157.4 (6)	97.3 (4)	0	0.12
Model 2		$S(22)-O(62)_D-H(3)_{1/2}\cdots O(51)_A-S(21)$	2.730 (4)	1.110 (9)	1.641 (9)	165.4 (7)	108.0 (6)	0	0.39

† A zero in this column indicates that the proton resides in a single-minimum potential well. ‡ Calculated assuming that the proton resides at the center of symmetry.

the two relevant orientations or variants, are provided in Fig. 4. (A list of atomic coordinates corresponding to these structures is available as supplementary material.†) An overlay of these two figures leads to Fig. 5, in which the overall *C*2/*c* symmetry of the structure is obtained. Comparing Figs. 3 and 4, it is apparent that the $P/S(1)O_4$ groups in the simple model correspond to the crystallographically distinct PO_4 and $S(1)O_4$ groups of the complex model, and similarly, that the $S(2)O_4$ tetrahedral groups in the simple model correspond to the crystallographically distinct $S(21)O_4$ and $S(22)O_4$ groups in the complex model of this structure. Moreover, the H(2) bond between O(2) and O(3) in the simple model, with proton sites H(21) and H(22), corresponds to two crystallographically distinct bonds in the complex model, H(2*a*) and H(2*b*), giving rise to four distinct proton sites. While the refinement indicated that the average of the occupancies at H(21*a*) and H(21*b*) was 0.25, and that at H(22*a*) and H(22*b*) was 0.75, it was impossible to determine unequivocally the occupancies in these four sites individually. The long S(21)—O(31) distance of 1.590 (10) Å, as compared to the S(1)—O(21) distance of 1.429 (11) Å, strongly suggested that O(31) serves as a donor in a bond with a single minimum potential well. Thus, the H(21) site in the H(2*a*) bond was assumed to be fully occupied, and the H(22) site in this bond to be unoccupied. This assumption, in turn, implies that that the H(21) and H(22) sites of the H(2*b*) bond should be equally occupied, with an occupancy factor of 0.5.

The greatest difference between the simple model and the locally ordered complex model lies in the region of the H(3) bond. In Model 1, neighboring SO_4 groups are related by a center of symmetry and are hence crystallographically equivalent. The higher symmetry leads to the situation in which placement of a hydrogen bond between one pair of O atoms, O(5) and O(6), linking the two sulfate anions, must be accompanied by a second hydrogen bond between a related pair of O atoms, O(5′) and O(6′), that links the same two sulfate anions (Fig. 2). In the locally ordered model, the symmetry element relating neighboring sulfate groups is absent, and thus two pairs of crystallographically distinct atoms are derivative from the O(5)–O(6) pair in the parent structure. These are O(51)–O(62) and O(52)–O(61). The H(3) proton links O(51)–O(62), bringing the two O atoms to a distance of 2.715 (5) Å from each other. The O(52) and O(61) atoms, in turn, move further apart. Thus, it appears that the H(3) proton leads to a localized breaking of the symmetry and is responsible for the high displacement parameters obtained at the O(5) and O(6) atoms when the simple high-symmetry model of

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† Supplementary data are available from the IUCr electronic archives (Reference: BS0004). Services for accessing these data are described at the back of the journal.

Table 8. *Sums of the bond valences at the oxygen atoms in* β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$

Model 1

Atom	ΣS†	ΣS(O—H)‡	ΣS(all)
O(1)	1.627	0.459	2.087
O(2)	1.617	0.434	2.051
O(3)	1.517	0.564	2.081
O(4)	2.146		2.146
O(5)	2.032	0.027	2.059
O(6)	1.844	0.096	1.940
		Average	2.06
		Average deviation	0.04

Model 2

Atom	ΣS†	ΣS(O—H)‡	ΣS(all)
O(1*a*)	1.601	0.459	2.060
O(1*b*)	1.654	0.459	2.113
O(21)	1.741	0.174	1.915
O(22)	1.506	0.760	2.226
O(31)	1.356	0.625	1.981
O(32)	1.731	0.493	2.224
O(41)	2.150		2.150
O(42)	2.088		2.088
O(51)	1.954	0.083	2.037
O(52)	2.063		2.063
O(61)	1.957		1.957
O(62)	1.637	0.308	1.945
		Average	2.07
		Average deviation	0.08

† Excluding the contributions of O—H bonds. ‡ Including the contributions of O—H bonds.

β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ was assumed. It is noteworthy that even in this model, only half of the SO_4–SO_4 neighbors along the chain are hydrogen bonded to one another.

Because of the low temperature at which the diffraction data were collected, it is unclear whether the disorder that gives rise to the overall *C*2/*c* symmetry in Model 2 is spatial or if it is temporal. That is, on the basis of the diffraction data alone, one cannot determine whether atoms jump back and forth between neighboring sites (presumably in a correlated fashion), or the structure is fixed in one or the other variant over some very short length scale. With respect to the P and S(1) atoms of Model 2, it is implausible that these atoms are temporally disordered. With respect to the S(21)O_4 and S(22)O_4 groups of Model 2, however, both temporal and spatial disorder are likely, and in this region Models 1 and 2 essentially describe the same structure, albeit using slightly different terms. The S(2)O_4 group of Model 1 is simply the spatial (and temporal) average of the S(21)O_4 and S(22)O_4 groups of Model 2. The exact orientation of the S(2)O_4 group in Model 2 will depend on (i) the presence or absence of an H(3) atom in the O(6)–O(5) bond, (ii) which of the two S(2)O_4 groups provides the donor O(62) atom, and (iii) the precise location of the H(2) atom, which, in turn, depends on (iv) whether the *X*(1) atom is an S atom or a P atom. The position of the Cs(2) atom, which has O(5) and O(6) atoms as rather close nearest neighbors (Table 5) and is 2.937 (8) Å away from the H(3) atom in Model 1, would also be influenced by the presence or absence of this proton. Accordingly, Cs(2) exhibits large displacement parameters in Model 1, and has been refined as a split atom in Model 2. In summary, one can conceive of a myriad of possible local configurations for the structure; in Model 2, which represents the most satisfactory fit to

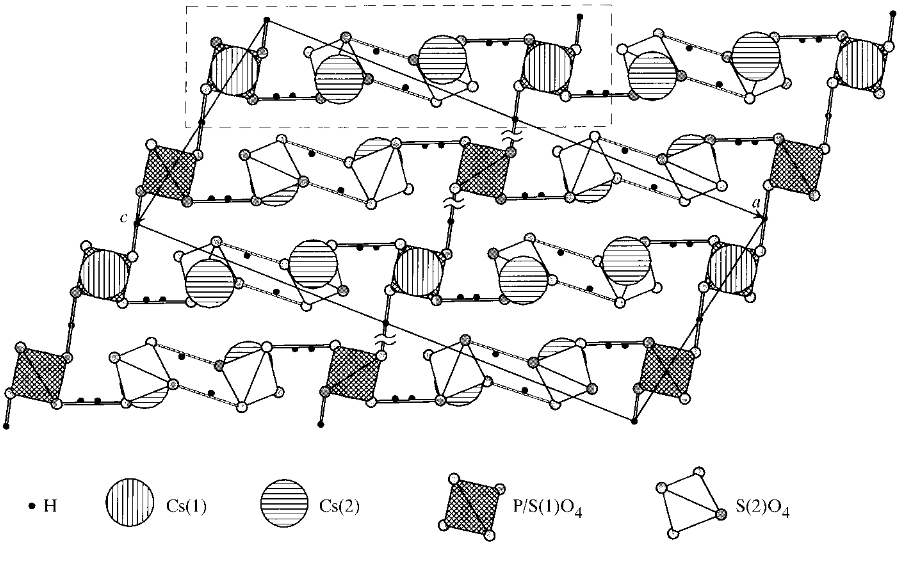

Fig. 2. The structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, Model 1, projected on (101). Hydrogen bonds between O atoms are shown. Bonds between O(6) and O(5) are drawn with dashes to indicate the less than full occupancy at the H(3) sites. Wavy lines that break hydrogen bonds indicate that one of the O atoms in the pair is not, in fact, shown. The region of the structure outlined with a dashed line is depicted in greater detail in Figs. 3–5.

the diffraction data of several models examined, we assume the superposition of two physically highly plausible local configurations.

5.2. *Coordination polyhedra*

The bond distances obtained in the caesium polyhedra and the sums of the bond valences at each of the Cs sites in the simple and complex models of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ are compared in Table 5. In both models, the Cs atoms are each coordinated by either 10 or 11 O atoms. In the case of the complex model, the Cs(1) atom can be coordinated by one of two slightly different polyhedra, depending on which local $P2/c$ variant the rest of the structure adopts. In a sense, the same is true of the Cs(2) atom; however, it shifts position to either Cs(21) or Cs(22) in parallel with the shifts in atom positions in the rest of the structure. The average bond distances in the Cs polyhedra, ~3.19 Å, and the sum of the bond valences, ~1.3, are reasonable in both models (Table 5).

The distances and angles determined in the XO_4 tetrahedra and the sum of the bond valences at each of the X-atom sites are compared for the two models in Table 6. An examination of the average X—O bond lengths and of the sum of the bond valences at the X-atom sites again reveals the self-consistency of each model, but does not lead to a preference of one model over the other. In the case of the simple model, the sum of the bond valences at the P/S(1) site is 5.50, in agreement with the refined occupancy of approximately 0.5 P and 0.5 S. Similarly, the sum of the bond valences at the S(2) site is 6.14, in agreement with the presumption that S fully occupies this site. The average X—O distance in the P/S(1)O_4 tetrahedron is 1.503 Å, whereas that in the S(2)O_4 tetrahedron is 1.468 Å. Again, these values are in good agreement with the chemical assignment of the X atoms. For the complex model, the sum of the bond valences at the P atom site is 5.15, whereas it is 5.82, 5.96 and 6.10 for the three S-atom sites. The bond valences used to obtain these sums were calculated assuming the occupancies given in Table 4; because of the chemical similarity between P and S, the valences of P—O and S—O bonds are virtually identical [compare equations (2) and (3)] and precise knowledge of X-atom occupancies is not necessary for meaningful bond-valence-sum calculations. The average X—O distances at these four sites are 1.524, 1.486, 1.482 and 1.469 Å, respectively, as would be expected for typical phosphate and sulfate groups. Differences between individual X—O distances are discussed below, in the context of hydrogen bonds formed by the O atoms.

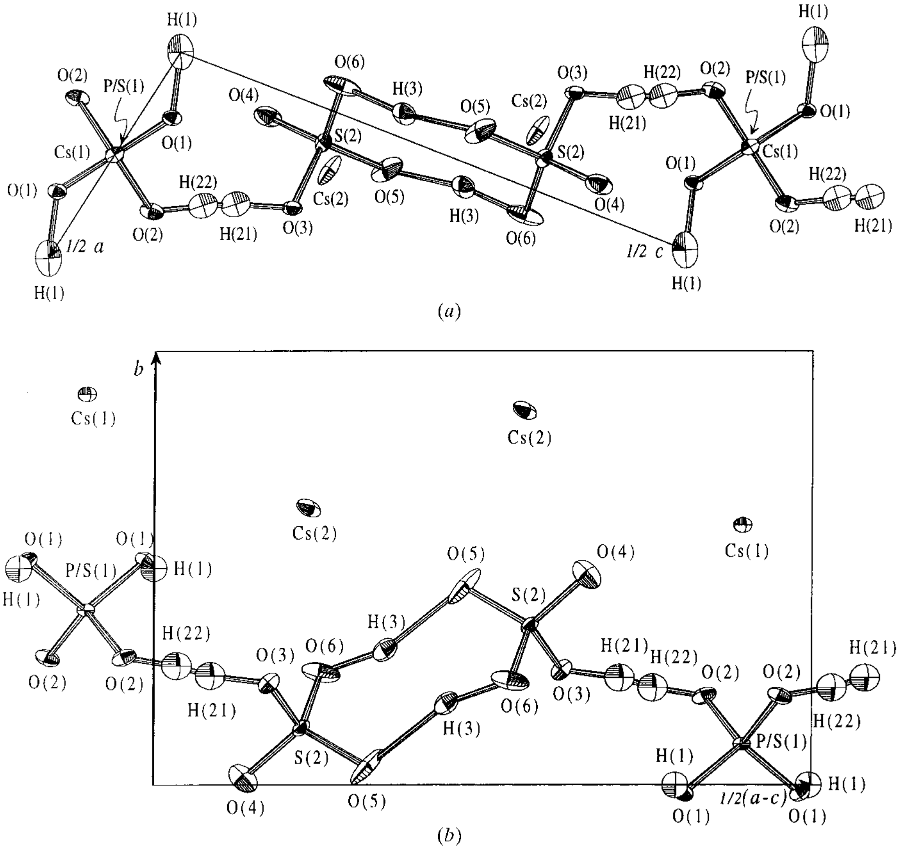

Fig. 3. Displacement-ellipsoid representations of the structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, Model 1, with a probability density of 50%. The region of the structure shown corresponds to that outlined with a dashed line in Fig. 2. (*a*) Projection on (010); (*b*) projection on (101).

5.3. *Hydrogen bonds and XO_4 geometry*

5.3.1. *P/S(1)O_4 group*. In the simple model of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, all O atoms of the P/S(1)O_4 group form hydrogen bonds, with O(1) atoms serving as mixed donor/acceptors and O(2) atoms serving as acceptors in the hydrogen bonds between O(2) and O(3). The corresponding phosphate and sulfate groups of the complex model also have hydrogen bonds involving all O atoms, and, again, O(1) serves as a mixed donor/acceptor. The X—$O(1)_{A/D}$ distance in both models is 1.506 (2) Å and the $O(1)_{A/D}\cdots O(1')_{A/D}$ distances are 2.456 (2) and 2.457 (2) Å. The hydrogen bond formed between them by H(1) has a single minimum and a linear O—H···O configuration. It is noteworthy that this bond, with an O···O distance of 2.474 (9) Å at room temperature, does not contract much upon cooling, and the persistence of the center of symmetry relating O(1) and O(1′) indicates that ferroelectricity should not be observed in β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$. This behavior contrasts that of CsH_2PO_4, in which a symmetric double-minima bond [between O(3) and O(3′)] of length 2.472 (2) Å exists at room temperature, and cooling induces a symmetry-breaking ferroelectric transition at 154 K (Matsunaga *et al.*, 1980).

The second hydrogen bond in which the P/S(1)O_4 group of the simple model participates, that between O(2) and O(3), is asymmetric and contains two minima in the potential well. Because the deeper minimum is close to O(3), *i.e.* the occupancy at H(21) is greater than at H(22), and because the (P,S)—O(2) distance is significantly shorter than the S(2)—O(3) distance (Table 6), the O(2) atom is identified as the acceptor and the O(3) atom as the donor. In the complex model of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, the parent P/S(1)$O_4$ group is (as described above) represented by the two independent tetrahedral units PO_4 and S(1)O_4. In analogy to the simple model, an asymmetric double-minima hydrogen bond exists between the O(22) atom of the PO_4 group and O(32) (Table 7). However, the occupancies obtained in the two minima are 0.5 each, and thus both the O(22) and O(32) atoms serve as mixed donor/acceptors. The longer P—O(22) bond relative to the S(22)—O(32) bond (Table 6) reflects differences in the nature of the X atom rather than in the nature of the hydrogen bonding at the O atom. In the case of the S(1)O_4 group, the second XO_4 group corresponding to

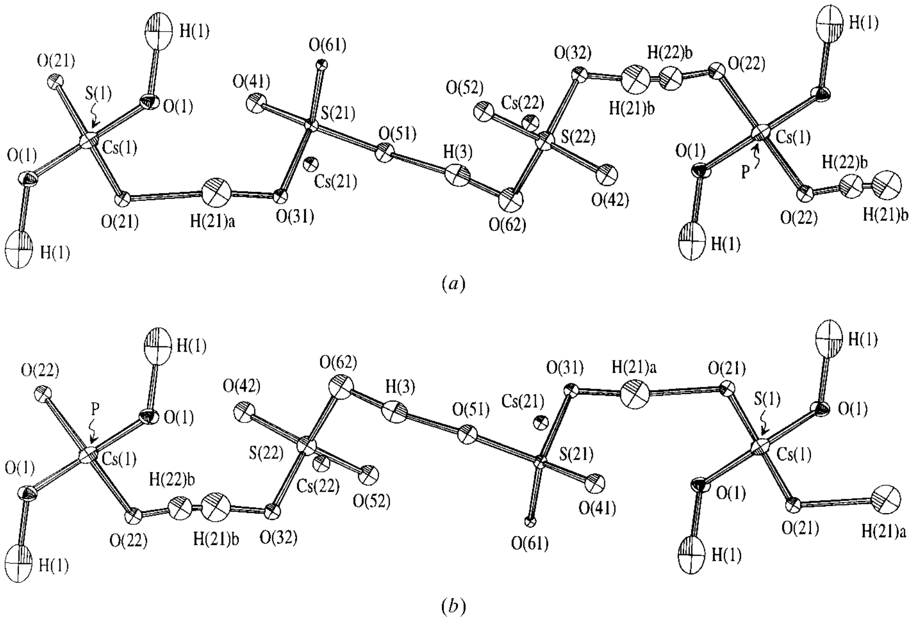

Fig. 4. Displacement-ellipsoid representations of the two variants of the structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, Model 2, with a probability density of 50%, projected on (101). Each variant has *P*2/*c* symmetry. Variant (*b*) can be obtained by applying the translation operation 1/2, 1/2, 0 to variant (*a*).

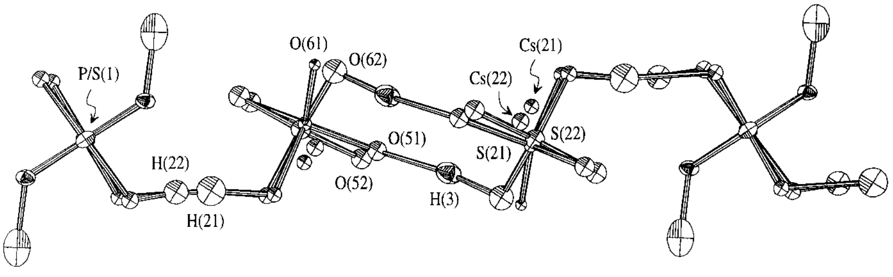

Fig. 5. A displacement-ellipsoid representation of the structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$, Model 2, with a probability density of 50%, projected on (101). This structure is essentially a superposition of the two variants shown in Fig. 4.

the parent P/S(1)O_4 anion of Model 1, the O(21) atom has a function quite similar to that of the O(2) atom of the simple model. It serves as an acceptor in the O(21)$\cdots$O(31) bond, as evidenced by the significantly greater length of S(21)—O(31) bond relative to the S(1)—O(21) bond.

5.3.2. *S(2)O₄ group*. The second tetrahedral unit of the simple model, the S(2)O_4 group, has one O atom, O(3), that is a donor in the H(2) hydrogen bond as discussed above. This atom retains its role as donor in the S(21)O_4 group of the complex model, but serves as a mixed acceptor/donor in the S(22)O_4 group as also discussed above. The key difference between the S(2)O_4 group of the simple model and the corresponding sulfate groups in the complex model is the nature of the O(5) and O(6) atoms. As noted earlier, the O(5) and O(6) atoms exhibited unusually large and anisotropic displacements when refined in the simple model. In addition, the lengths of the S(2)—O(5) and S(2)—O(6) bonds hardly seem influenced by the presence of a proton at H(3) that should link the two O atoms. Normally, X—O_D and even X—O_A distances are measurably longer than X—O distances. Thus, at best, O(5) can be described as a 'weak' acceptor and O(6) as a 'weak' donor in the simple model. In contrast, in the complex model, the S(21)O_4 and S(22)O_4 tetrahedra take on orientations that bring the O(51) and O(62) atoms close to one another such that a more typical hydrogen-bond length is achieved [2.715 (5) Å], while the now crystallographically independent O(52) and O(61) atoms become quite distant from one another. Concurrently, the bond distances in the S(22)O_4 group reflect the assignment of the O(62) atom as a donor in a hydrogen bond, that is, the S(22)—O(62) bond is significantly longer than the other S—O bonds in this anion group, and the X—O—H angles take on more realistic values (Table 7).

6. Conclusions

The structure of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ has been refined using two models, one in which both the local and global symmetry is *C*2/*c* (the simple model), and one in which the structure has local symmetry *P*2/*c* but global symmetry *C*2/*c*. Refinement of relevant site occupancies in both models leads to the conclusion that, for the crystal examined, $x = 0.500$ (6). Both refinements yielded reasonable residuals and are self-consistent in terms of a bond-valence analysis (Table 8). The somewhat unusual geometry of the O(5)$\cdots$H(3)—O(6) bond obtained in the refinement of the simple model suggests that the locally ordered (globally disordered) model more accurately represents the real structure, particularly with respect to the S(2)O_4 group. This sulfate anion takes on the S(22)O_4 configuration of Model 2 when the O(6) atom serves as a proton donor [becoming O(62)], and takes on the S(21)O_4 configuration when no proton is present or when O(5) serves as an acceptor [becoming O(51)]. At the low temperature at which the neutron diffraction data were collected, it is unclear whether the disorder observed about S(2)O_4 is temporal or spatial in nature. However, the structure at room temperature surely undergoes temporal disorder, with S(2)O_4 anions changing orientations between the S(21)O_4 and S(22)O_4 configurations as protons hop back and forth between the two O(5)—O(6) bonds linking neighboring S(2)O_4 groups. In addition, it is quite plausible that protons also jump back and forth between S(2)O_4 groups of neighboring chains. Such proton hopping would explain the much higher room-temperature conductivity of β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$ as compared to α-$Cs_3(HSO_4)_2[H_2PO_4]$, which has a similar structure but which has no partially occupied proton sites (Haile, Lentz *et al.*, 1995).

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References

Alig, H., Lösel, J. & Trömel, M. (1994). *Z. Kristallogr.* **209**, 18–21.

Baranov, A. I., Shuvalov, L. A. & Shchagina, N. M. (1982). *JETP Lett.* **36**, 459–462.

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* A**30**, 129–147.

Belushkin, A. V., David, W. I. F., Ibberson, R. M. & Shuvalov, L. A. (1991). *Acta Cryst.* B**47**, 161–166.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Dowty, E. (1997). *ATOMS*. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Haile, S. M., Calkins, P. M. & Boysen, D. (1997). *Solid State Ion.* **97**, 145–151.

Haile, S. M., Calkins, P. M. & Boysen, D. (1998). *J. Solid State Chem.* **139**, 373–387.

Haile, S. M., Kreuer, K.-D. & Maier, J. (1995). *Acta Cryst.* B**51**, 680–687.

Haile, S. M., Lentz, G., Kreuer, K.-D. & Maier, J. (1995). *Solid State Ion.* **77**, 128–134.

Ichikawa, M. (1978). *Acta Cryst.* B**34**, 2074–2080.

Lundgren, J.-O. (1982). Report UUIC-B13-4-05. Institute of Chemistry, University of Upsala, Sweden.

McMullan, R. K., Epstein, J., Ruble, J. R. & Craven, B. M. (1979). *Acta Cryst.* B**35**, 688–691.

Matsunaga, H., Itoh, K. & Nakamura, E. (1980). *J. Phys. Soc. Jpn*, **48**, 2011–2014.

Pawlowski, A., Pawlaczyk, Cz. & Hilczer, B. (1990). *Solid State Ion.* **44**, 17–19.

Sears, V. F. (1993). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 383–391. Dordrecht: Kluwer.