Synthesis, structure, and properties of compounds in the NaHSO4–CsHSO4 system. 1. Crystal structures of Cs2Na(HSO4)3 and CsNa2(HSO4)3

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Synthesis, Structure, and Properties of Compounds in the NaHSO$_4$−CsHSO$_4$ System. 1. Crystal Structures of Cs$_2$Na(HSO$_4$)$_3$ and CsNa$_2$(HSO$_4$)$_3$

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Exploratory synthesis in the NaHSO$_4$−CsHSO$_4$ system, aimed at discovering novel proton conducting solids, resulted in the new compounds CsNa$_2$(HSO$_4$)$_3$ and Cs$_2$Na(HSO$_4$)$_3$. Single-crystal X-ray diffraction (performed at room temperature) revealed CsNa$_2$(HSO$_4$)$_3$ to crystallize in the cubic space group $P2_13$ with lattice parameters $a = 10.568(2)$ Å and $Z = 4$, whereas Cs$_2$Na(HSO$_4$)$_3$, studied by both single-crystal neutron and X-ray methods, crystallizes in the hexagonal space group $P6_3/m$. The latter compound has lattice parameters $a = 8.5712(17)$ and $c = 9.980(2)$ Å, and $Z = 2$. The unit cell volumes are 1180.4(4) and 634.9-(2) Å^3, respectively, giving calculated densities of 2.645 and 3.304 mg m^{-3}. Refinement using all observed reflections yielded a weighted residual, $R_w(F^2)$, of 0.0515 based on F^2 X-ray values for CsNa$_2$(HSO$_4$)$_3$. For Cs$_2$Na(HSO$_4$)$_3$ the analogous X-ray and neutron values were 0.0483 and 0.1715, respectively. Both structures contain a single, crystallographically distinct, asymmetric hydrogen bond (as confirmed by NMR investigations) and unique, three-membered (HSO$_4$)$_3$ rings. The geometric match between the NaO$_6$ octahedra and the rings suggests the sodium polyhedra may serve to template the (HSO$_4$)$_3$ unit. In CsNa$_2$(HSO$_4$)$_3$ the rings form a distorted cubic close-packed array. The Cs atoms are located within the "octahedral" sites of this array, and the Na atoms, within the "tetrahedral" sites. The rings in Cs$_2$Na(HSO$_4$)$_3$ are linked together by NaO$_6$ octahedra to form infinite Na(HSO$_4$)$_3$ chains that extend along [001]. The hexagonal compound exhibits disorder about the sulfate tetrahedron that suggests a $P6_3/m \rightarrow P6$ phase transition may occur upon cooling.

Introduction

Many solid acid sulfates and selenates undergo structural phase transitions that lead to high proton conductivity at slightly elevated temperatures.[1−4] In particular, compounds of general formula MHXO$_4$, where M = alkali metal or ammonia and X = sulfur or selenium, are well-known to exhibit such behavior, so long as the M cation is of "sufficiently" large size.[5] In the present work, we have undertaken a systematic study of the NaHSO$_4$−CsHSO$_4$ system with the objective of quantifying the relationship between cation size and superprotonic phase transitions. The ultimate goal of these studies is to enable one to tune phase transitions and high-temperature behavior via judicious control of material chemistry. In this first part in a two-part series, we report the structures of two new cesium−

sodium solid acids. Their proton transport properties and thermal behavior are reported in part 2.[6]

Sample Preparation and Preliminary Analysis

Single crystals of CsNa$_2$(HSO$_4$)$_3$ and Cs$_2$Na(HSO$_4$)$_3$ were grown from aqueous solutions of Cs$_2$CO$_3$, Na$_2$CO$_3$, and H$_2$SO$_4$, with Cs/Na/SO$_4$ molar ratios of 1:1:2 and 7:3:10, respectively. Further details are presented elsewhere.[6] The crystal of CsNa$_2$(HSO$_4$)$_3$ used for X-ray diffraction analysis and that of Cs$_2$Na(HSO$_4$)$_3$ used for neutron diffraction analysis were utilized in as-synthesized form and had the dimensions 0.3 × 0.3 × 0.45 mm^3 and 2.5 × 2.5 × 5.5 mm^3, respectively. A specimen of Cs$_2$Na(HSO$_4$)$_3$ was ground to an ellipsoid shape ($\sim$0.1 × 0.1 × 0.2 mm^3) for X-ray data analysis in order to minimize errors due to adsorption effects. This additional effort was taken for Cs$_2$Na(HSO$_4$)$_3$ because of difficulties in unambiguously resolving the space group, as discussed below. The Cs$_2$Na(HSO$_4$)$_3$ compound was also studied by polarized light microscopy using a Nikon Optiphot Pol microscope, again, to aid in space group assignment. Thin platelets, oriented perpendicular to

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(4) Pawlaczyk, Cz.; Salman, F. E.; Pawlowski, A.; Czapla, Z.; Pietraszko, A. *Phase Transitions* **1986**, *8*, 9−16.

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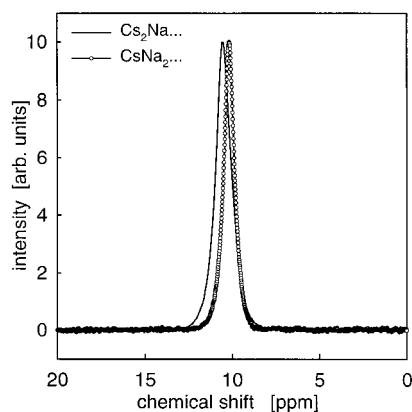(6) Chisholm, C. R. I.; Cowan, L. A.; Haile, S. M. Under preparation.

Crystal Structures of Cs₂Na(HSO₄)₃ and CsNa₂(HSO₄)₃

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Figure 1. Proton NMR spectra of Cs₂Na(HSO₄)₃ and CsNa₂-(HSO₄)₃.

the *c* axis, were cut and polished. Examination under crossed polarizers in orthoscopic and conoscopic illumination showed the crystal to be optically inactive (within the measurement limits), a result consistent with either of the two hexagonal space groups indicated by the diffraction data.

NMR Spectroscopy

Proton NMR measurements were performed on single-crystal samples after they were ground into a powder and dried in a desiccator at ~105 °C for 24 h. The NMR spectrum for the $Cs_2Na(HSO_4)_3$ compound was taken on a Bruker AM 300 MHz spectrometer, heavily modified for solid NMR experiments, at a sample spinning rate of 12.5 kHz. A Bruker DSX 500 MHz NMR spectrometer was used to characterize the proton environment in the $Cs_2Na(HSO_4)_3$ compound, with a sample spinning rate of 12 kHz. Both spectrometers employed a 4 μs, 90° pulse, with the chemical shift referenced to tetramethylsilane (TMS). The results of the measurements are presented in Figure 1. The presence of a single peak in the spectra of both compounds indicates that in each there is only one type of proton site. The chemical shifts, 10.16 ppm for CsNa₂-(HSO₄)₃ and 10.58 for Cs₂Na(HSO₄)₃, and peak widths are comparable, suggesting the proton environments in the two compounds are similar.

Structure Determination

Experimental Procedure. Single-crystal X-ray diffraction intensity data were obtained at room temperature on a Syntex 4-circle diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) for both $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$. In the case of $CsNa_2(HSO_4)_3$, the lattice was identified as primitive cubic [$a = 10.568(2)$ Å] in the preliminary analysis. Examination of the full data set showed the 001 peaks, for which $l \neq 2n$, to be systematically absent, and the peak intensities were consistent with those of the Laue group $m\bar{3}$. Together, these imply space group $P2_13$, a result confirmed by the subsequent structure determination and refinement. The second compound, $Cs_2Na(HSO_4)_3$, was found to be hexagonal ($a = 8.5712(17)$ and $c = 9.980(2)$ according to the X-ray data) with diffraction symbol 6/m $P6_3$- -. In contrast to the result for the cubic compound, the final structure refinement of $Cs_2Na(HSO_4)_3$ using X-ray data alone did not allow us to unambiguously identify

the space group, that is, distinguish between space groups $P6_3$ and $P6_3/m$. In an attempt to address this question, and the related question of the location of the protons, $Cs_2Na(HSO_4)_3$ was also studied by single-crystal neutron diffraction methods. Neutron data were collected on the four-circle diffractometer at beam port HB2A of the high flux isotope reactor at Oak Ridge National Laboratory. The neutron beam was monochromated using germanium (133) planes in reflection geometry, for a wavelength of 1.0037 Å, as calibrated against KCl (6.2910 Å). Table 1 provides the complete data collection parameters for the three diffraction experiments, as well as selected crystallographic data and parameters related to the refinements.

Structure Solution. *CsNa₂(HSO₄)₃.* The structure of CsNa₂(HSO₄)₃ was solved by first finding the Cs, S, and Na atoms via direct methods and then O atoms from successive Fourier difference maps. In this manner, one Cs, two Na atoms, and one SO₄ group were found in the asymmetric unit, yielding a chemical formula consistent with the chemical analysis. An examination of the intertetrahedral O—O bond lengths and the S—O bond lengths indicated the presence of a hydrogen bond between the O(1) and O(2) oxygen atoms, with O(1) serving as the donor (the S—O(1) distance is signficantly longer than the remaining S—O bond lengths; see Table 4). A peak in the Fourier difference map located between these two atoms provided initial proton coordinates. Free refinement of the proton coordinates led to an unreasonably short O(1)—H distance, and thus its position was restrained to lie 1.00 ± 0.05 Å from O(1). This value corresponds to the expected distance based on the O(1)···O(2) distance of ~2.7 Å and the correlation between O···O and O—H distances in hydrogen bonds.[7] Introduction of the H(1) proton in this manner reduced the weighted residual, $R_w(F^2)$, from ~0.057 to ~0.052. Refinements with alternative restraints for the hydrogen bond led to equally acceptable geometries but poorer residuals.

In the final stages of the refinement, anisotropic thermal parameters were employed for all non-hydrogen atoms, and a fixed isotropic parameter of $U_{iso} = 0.05$ Å² (a value approximately twice that of the oxygen atoms) was emoployed for the hydrogen atom. The correctness of the handedness of the structure was tested by refining a structural model in which atomic coordinates were the inverse of those of the original model. This led to a substantial increase in the residuals; for example, $R_w(F^2)$ rose from ~0.52 to ~0.89. The possiblity of racemic twinning was explored using the twin refinement feature of SHELXL in which two inversion-related variants are taken to contribute to the diffraction intensity. The weight fraction of the inverted twin refined to a value of zero, and thus the crystal was taken to be untwinned, with coordinates as established from the original structure determination. The crystallographic origin was refined via the procedure established by Flack[8] and implemented in SHELXL. In addition, the scale factor and an overall extinction parameter were refined. The final residuals, based on 664 independent reflections, were $R_w(F^2) = 0.0515$ and $R(F) = 0.0286$. The data were weighted as described in

(7) Ichikawa, M. *Acta Crystallogr.* **1978**, *B34*, 2074–2080.
(8) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 867–881.

Table 1. Crystal Data, Data Collection Parameters, Data Refinement Parameters, and Other Experimental Details for the Structure Determination and Refinement for $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$

Crystal Data			
compound name	$CsNa_2(HSO_4)_3$	$Cs_2Na(HSO_4)_3$	$Cs_2Na(HSO_4)_3$
empirical formula	$H_3CsNa_2O_{12}S_3$	$H_3Cs_2NaO_{12}S_3$	$H_3Cs_2NaO_{12}S_3$
formula weight	1880.38	1160.02	1160.02
temperature	298(2) K	298(2) K	300(2) K
crystal system	cubic	hexagonal	hexagonal
space group	$P2_13$	$P6_3/m$	$P6_3/m$
unit cell dimensions	$a = 10.568(2)$ Å	$a = 8.5712(17)$ Å	8.580(2) Å
		$c = 9.980(2)$ Å	9.953(2) Å
volume	1180.4(4) Å^3	634.9(2) Å^3	634.5(3) Å^3
Z	4	2	2
density (calculated)	2.645 mg/m^3	3.034 mg/m^3	3.035 mg/m^3
absorption coefficient	3.795 mm^{-1}	5.929 mm^{-1}	0.494 mm^{-1}
$F(000)$	896	536	536
crystal size	$0.3 \times 0.3 \times 0.45$ mm^3	$0.1 \times 0.1 \times 0.2$ mm^3	$5.5 \times 2.5 \times 2.5$ mm^3
crystal color	colorless	colorless	colorless
crystal mounted	on glass fiber with epoxy	on glass fiber with epoxy	on Al fiber with epoxy
no. of reflections for cell determination	243 ($3.9° < \Theta < 16.3°$)	78 ($4.1° < \Theta < 16.0°$)	30 ($18° < \Theta < 32°$)
Data Collection			
radiation	X-ray Mo Kα	X-ray Mo Kα	neutron (reactor)
wavelength	0.71070 Å	0.71070 Å	1.0037 Å
instrument	Syntex four-circle	Syntex four-circle	beamline HB2a, HFIR′
data collection method	$\Theta{-}2\Theta$ scans	$\Theta{-}2\Theta$ scans	$\Theta{-}2\Theta$ scans
absorption correction method	empirical, psi scan	empirical, psi scan	none
maximum and minimun trans	1.00 and 0.73	1.00 and 0.97	not applicable
Θ range for data collection	$2.73{-}29.99°$	$2.74{-}29.99°$	$3{-}50°$
index ranges	$0 \leq h \leq 14, 0 \leq k \leq 14,$ $0 \leq l \leq 14$	$0 \leq h \leq 12, -12 \leq k \leq 10,$ $-13 \leq l \leq 14$	$0 \leq h \leq 10, 0 \leq k \leq 11,$ $-15 \leq l \leq 0$
reflections collected	1976	3685	956
independent reflections	664 [R(int) = 0.0747]	653 [R(int) = 0.0383]	823 [R(int) = 0.063]
significant reflections	627 [$I > 2\sigma(I)$]	576 [$I > 2\sigma(I)$]	247 [$I > 3\sigma(I)$]
standards	3	3	3
deviation of standards	-1.1%	-6.8%	0%
decay correction	applied	applied	not applied
Refinement			
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
final R indices (sig data)	R1 = 0.0250, wR2 = 0.0504	R1 = 0.0286, wR2 = 0.0466	R1 = 0.068
R indices (all data)	R1 = 0.0286, wR2 = 0.0515	R1 = 0.0356, wR2 = 0.0483	R1 = 0.2357, wR2 = 0.1715
goodness-of-fit on F^2	1.118	1.168	1.385
reflections used in refinement	664	653	813
refined parameters	59	46	51
restraints	1	1	none
weighting scheme	$[\sigma^2(F_o^2) + (0.0097P)^2]^{-1}$ $P = (F_o^2 + 2F_c^2)/3$	$[\sigma^2(F_o^2) + (0.0101P)^2 + 0.7879P]^{-1}$ $P = (F_o^2 + 2F_c^2)/3$	$1/(\sigma^2(F) + 0.004F^2)$
(δ/σ) max and mean	0.00 and 0.00	0.029 and 0.003	0.1 (max); no mean
largest diff peak and hole	0.701 and -0.593 e/Å^3	0.488 and -0.351 e/Å^3	$+7$ and -7% of max.
anisotropic thermal parameters	all non-hydrogen	all non-hydrogen	all atoms
absolute structure parameter	$-0.05(3)$	not applicable	not applicable
extinction coefficient	0.0272(17)	0.0166(7)	not applied
sources of atomic scattering factors	*Int. Tables*[a]	*Int. Tables*[a]	*Int. Tables*[a]
treatment of H atoms	restrained (see text)	restrained (see text)	free refinement
Computer Programs			
structure solution	SHELXS86	SHELXS86	X-ray results
structure refinement	SHELXL97	SHELXL97	UPALS
structure depiction	ATOMS	ATOMS	ATOMS

[a] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4, Table 2.2A, pp 128–134 (Present distributor: Kluwer Academic Publishers, Dordrecht).

Table 1, and refinements were carried out against F^2 values. All calculations were performed with the SHELXS and SHELXL programs,[9,10] using the Wing interface.[11]

$Cs_2Na(HSO_4)_3$. As in the case of $CsNa_2(HSO_4)_3$, the structure of $Cs_2Na(HSO_4)_3$ was solved from the X-ray data by first finding the Cs, S, and Na atoms via direct

methods and then the O atoms from successive Fourier difference maps. This X-ray structural model served as a starting point for the neutron data analysis. The asymmetric unit of $Cs_2Na(HSO_4)_3$ contains one Cs atom, one Na atom, one S atom, and three O atoms, with the third of these oxygen atoms equally distributed over two neighboring positions. The multiplicities of the various sites lead to the formula as given, which is, again, consistent with the chemical analysis.

As with the first compound, examination of the intertetrahedral O–O bond lengths was used to locate potential hydrogen bonds. In the early stages of the

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(10) Sheldrick, G. M. *SHELX97*; Institüt für Anorganische Chemie der Universität: Göttingen, Germany, 1998.
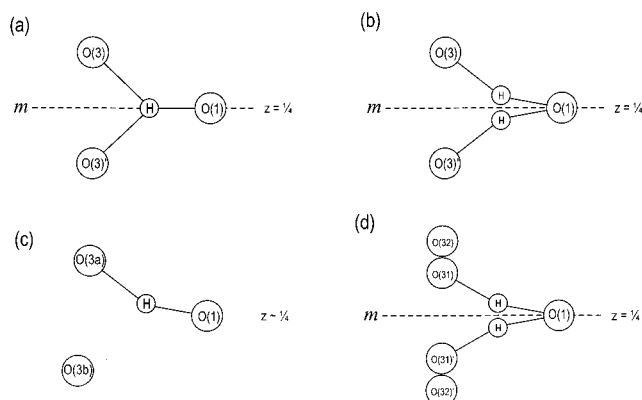(11) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

Figure 2. Schematic representation of possible hydrogen bond geometries in Cs₂Na(HSO₄)₃: (a) in the space group $P6_3/m$ with the hydrogen residing on the mirror plane; (b) in the space group $P6_3/m$ with the hydrogen displaced from the mirror plane; (c) in the space group $P6_3$, in which there is no mirror plane; (d) in the space group $P6_3/m$ with the hydrogen dispaced from the mirror plane and the O(3) atom split over two neighboring sites. The geometry shown in part d reflects the final model adopted.

refinement, in which the third oxygen atom, O(3), was not yet split, two suggestive O–O bond lengths were apparent, O(1)···O(2) at 2.96 Å and O(1)···O(3) at 3.02 Å. Fourier difference maps constructed using the neutron data clearly showed a peak between the latter two oxygen atoms, and none between O(1) and O(2), despite the shorter O–O distance. Furthermore, as discussed above, the NMR data indicated that there is a single, crystallographically distinct proton site in Cs₂Na-(HSO₄)₃, and thus, the possibility of partial proton occupation of a site between O(1) and O(2) was ruled out.

Several possible geometries were examined for the O(1)–H···O(3) hydrogen bond, shown schematically in Figure 2. As stated above, O(3) was initially placed on a single, fully occupied general position with multiplicity 12 in space group $P6_3/m$. In this same space group, which contains a mirror plane at $z = ^1/_4$, the O(1) atom (with z coordinate also $^1/_4$) lies on a special position of multiplicity 6. To obtain a charge-balanced chemical formula, these observations imply that the hydrogen atom serving to bond O(1) and O(3) must either also lie on the mirror plane on a fully occupied special position (Figure 2a) or be displaced from it onto a $^1/_2$-occupied general position (Figure 2b). In the case of space group $P6_3$, there are no mirror planes and thus O(1) is located on a general position and its multiplicity remains at 6. The loss of the mirror symmetry lowers the multiplicity of the O(3) atom, now O(3a), from 12 to 6 also. Therefore, to obtain the same general structure, an additional oxygen atom must be introduced, O(3b). These atoms, O(3a) and O(3b), are not related by symmetry, as the corresponding atoms would be in the higher space group. Accordingly, a single proton may link, for example, O(1) and O(3a), whereas O(3b) may be far from any proton (Figure 2c). Furthermore, the proton between O(1) and O(3a) now lies in a general position with full occupancy. A fourth possibility (Figure 2d) is that the structure crystallizes in the higher symmetry space group $P6_3/m$, that the proton is displaced from the mirror plane (occupancy = $^1/_2$), and that this displacement causes the O(3) atom to be split over two independent positions, O(31) and O(32). It is in this manner

(model of Figure 2c as compared to the other three models) that the precise location of the proton is closely tied to the space group.

Refinements of the structural parameters were pursued in the various models described above for both data sets (analyzed independently). In general, refinements in $P6_3$ suffered from higher residuals (particularly for the neutron data) and larger correlations between crystallographic parameters. Moreover, for all models and both data sets, a rather short S–O bond was obtained for the oxygen that should serve as acceptor in the O···O hydrogen bond. This was particularly so in space group $P6_3/m$ in models containing a single O(3) site. In contrast, the bond distance between sulfur and the donor oxygen atom was rather typical (longer by about 0.13 Å than an S–O bond which is not influenced by protons). The centrosymmetric space group also yielded highly anisotropic thermal displacement parameters for the O(3) atom, in models in which this atom was constrained to reside on the mirror plane. Ultimately, the model that yielded the best compromise between sulfate group geometry, hydrogen bond geometry, thermal ellipsoid shape, and residuals was that shown in Figure 2d, that is, in space group $P6_3/m$ with O(3) split equally over two symmetry independent positions, O(31) and O(32), and H(1) residing at a $^1/_2$-occupied site, slightly displaced from the mirror plane. In an attempt to improve the sulfate group geometry, refinements in which the O(1), O(2), and even S atoms were similarly displaced from the mirror plane (and given $^1/_2$ occupancy) were pursued. In this case, the distance between neighboring sites was hardly greater than the esd's of those values, and such refinements were abandoned.

In the final stages of the refinement, anisotropic thermal displacement parameters were employed for all atoms, except, in the case of the X-ray data, for the hydrogen atom. Scale factors were varied in both refinements, and an overall extinction parameter was employed to model the X-ray data. The final residuals obtained from the X-ray data, based on 653 independent reflections, were $R_w(F^2) = 0.0483$ and $R(F) = 0.0356$. The analogous $R_w(F^2)$ value for the neutron experiment, based on 823 independent reflections, was 0.1715. The data were weighted as described in Table 1, and refinements were carried out against F^2 values. Neutron data analysis was performed using the UPALS[12] program, whereas all calculations involving the X-ray data were conducted with the SHELXS and SHELXL programs.[9,10]

Results

Atomic coordinates and thermal parameters for Cs₂-Na(HSO₄)₃ are given in Tables 2 and 3, respectively. Interatomic distances for the cation polyhedra are listed in Table 4, as are the interatomic angles for the SO₄ tetrahedra. The corresponding results for CsNa₂(HSO₄)₃, as determined from both X-ray and neutron data, are provided in Tables 5–7. In Table 8 the geometric features of the hydrogen bonds in each of the structures are presented.

To provide an internal consistency check on the results, bond valence sums were calculated for both

(12) Lundgren, J.-O. Report UUIC-B13-4-05; Institute of Chemistry, University of Uppsala: Uppsala, Sweden, 1982.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Cubic Compound $CsNa_2(HSO_4)_3$

	site	symmetry	x	y	z	$U(eq)^a$
Cs	4a	.3.	0.05223(2)	0.94777(2)	0.44777(2)	0.0226(1)
Na(1)	4a	.3.	0.1745(2)	0.3255(2)	0.6745(2)	0.0242(6)
Na(2)	4a	.3.	0.1024(2)	0.1024(2)	0.1024(2)	0.0183(6)
S	12b	1	0.21156(8)	0.62174(9)	0.51004(9)	0.0160(2)
O(1)$_D$	12b	1	0.2252(3)	0.5734(3)	0.3698(3)	0.0256(7)
O(2)$_A$	12b	1	0.0790(3)	0.6584(3)	0.5252(3)	0.0228(6)
O(3)	12b	1	0.2972(3)	0.7282(3)	0.5134(3)	0.0296(7)
O(4)	12b	1	0.2480(3)	0.5202(3)	0.5919(4)	0.0325(8)
H(1)	12b	1	0.188(5)	0.495(5)	0.388(7)	0.050

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3. Anisotropic Displacement Parameters ($Å^2$) for the Cubic Compound $CsNa_2(HSO_4)_3$^{a}

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cs	0.0226(2)	0.0226(2)	0.0226(2)	0.0031(1)	−0.0031(1)	−0.0031(1)
Na(1)	0.0242(6)	0.0242(6)	0.0242(6)	0.0009(7)	−0.0009(7)	0.0009(7)
Na(2)	0.0183(6)	0.0183(6)	0.0183(6)	0.0004(6)	0.0004(6)	0.0004(6)
S	0.0137(4)	0.0148(4)	0.0194(4)	0.0006(4)	−0.0007(3)	−0.0028(3)
O(1)$_D$	0.025(1)	0.031(2)	0.021(1)	−0.007(1)	0.009(1)	−0.005(1)
O(2)$_A$	0.017(1)	0.028(1)	0.024(1)	−0.002(1)	0.004(1)	0.002(1)
O(3)	0.027(1)	0.023(2)	0.039(2)	−0.004(1)	−0.002(1)	−0.012(1)
O(4)	0.033(2)	0.026(2)	0.038(2)	0.011(1)	−0.004(1)	0.003(1)

^{a} The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$.

Table 4. Coordination Polyhedra in the Cubic Compound $CsNa_2(HSO_4)_3$

(a) Bond Lengths (Å) in the Cesium Polyhedron and Sodium Octahedra^a

Cs−O(2)$_A$	3.178(3)	Na(1)−O(4)	2.365(4)	Na(2)−O(3)	2.284(3)
Cs−O(4)	3.260(4)	Na(1)−O(1)$_D$	2.555(3)	Na(2)−O(2)$_A$	2.418(3)
Cs−O(3)	3.300(4)	mean	2.315	mean	2.460
mean	3.246				

(b) Interatomic Distances (Å) and Angles (deg) in the Sulfate Tetrahedron

S	distance	angle	distance	angle	distance	angle	distance
O(4)	1.432(3)						
O(3)	1.444(3)	113.6(2)	2.406(5)				
O(2)$_A$	1.462(3)	113.0(2)	2.413(5)	113.0(2)	2.424(4)		
O(1)$_D$	1.574(3)	107.5(2)	2.426(5)	102.6(2)	2.358(5)	106.07(18)	2.427(4)
	⟨1.478⟩	O(4)	O(4)	O(3)	O(3)	O(2)	O(2)

^{a} All bonds have a multiplicity of three.

Table 5. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2$) for the Hexagonal Compound $Cs_2Na(HSO_4)_3$^{a}

	site	symmetry	x	y	z	$U(eq)$
Cs	4f	3..	0.6667	0.3333	0.00613(3)	0.0421(2)
			0.6667	*0.3333*	*0.0061(4)*	*0.0800(1)*
Na	2b	m..	0	0	0	0.0304(5)
			0	*0*	*0*	*0.0590(2)*
S	6h	m..	0.0272(1)	0.7202(1)	0.25	0.0254(2)
			0.291(1)	*0.7200(6)*	*0.25*	*0.0508(1)*
O(1)$_D$	6h	m..	−0.1815(4)	0.6294(5)	0.25	0.054(1)
			−0.1810(4)	*0.6301(4)*	*0.25*	*0.0794(1)*
O(2)	6h	m..	0.0641(5)	0.5762(4)	0.25	0.056(1)
			0.0628(4)	*0.5757(4)*	*0.25*	*0.0901(1)*
O(31)$_A$^{b}	12i	1	0.1098(7)	0.8639(7)	0.1547(5)	0.035(1)
			0.1122(8)	*0.8648(6)*	*0.1568(6)*	*0.0766(3)*
O(32)^b	12i	1	0.0650(9)	0.7879(9)	0.1107(5)	0.046(1)
			0.0656(9)	*0.7912(8)*	*0.1114(6)*	*0.1226(4)*
H^b	12i	1	−0.217(9)	0.706(8)	0.208(6)	0.050
			−0.2201(8)	*0.7181(8)*	*0.2190(9)*	*0.0810(5)*

^{a} U(eq) is defined as one-third of the trace of the orthogonalized U^{ij} tensor. Coordinates as determined from the X-ray data analysis are given in the first row, and those from the neutron data analysis are given in italics in the second row. ^{b} Site occupancy of $^1/_2$

structures. The valences of the Cs−O, Na−O, and S−O bonds were determined according to

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

$$S(Na-O) = \exp[(1.803 - d_{Na-O})/0.37] \qquad (2)$$

and

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

where d_{Cs-O}, d_{Na-O}, and d_{S-O} are the cesium-to-oxygen, sodium-to-oxygen, and sulfur-to-oxygen distances, re-

Table 6. Anisotropic Displacement Parameters (Å²) for the Hexagonal Compound $Cs_2Na(HSO_4)_3$[a]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cs	0.0470(2)	0.0470(2)	0.0325(2)	0	0	0.0235(1)
	0.061(1)	*0.061(1)*	*0.059(2)*	*0.000*	*0.000*	*0.030(1)*
Na	0.0336(8)	0.0336(8)	0.024(1)	0	0	0.0168(4)
	0.046(2)	*0.046(2)*	*0.040(4)*	*0.000*	*0.000*	*0.023(1)*
S	0.0257(5)	0.0206(4)	0.0333(5)	0	0	0.0141(4)
	0.036(2)	*0.030(2)*	*0.052(3)*	*0.000*	*0.000*	*0.017(2)*
O(1)$_D$	0.025(2)	0.029(2)	0.107(3)	0	0	0.012(1)
	0.037(1)	*0.042(2)*	*0.121(3)*	*0.000*	*0.000*	*0.019(1)*
O(2)	0.040(2)	0.028(2)	0.107(3)	0	0	0.022(2)
	0.050(2)	*0.038(1)*	*0.127(3)*	*0.000*	*0.000*	*0.028(1)*
O(31)$_A$	0.037(3)	0.028(3)	0.037(3)	0.008(2)	−0.001(2)	0.015(2)
	0.056(3)	*0.043(3)*	*0.055(3)*	*0.012(2)*	*0.006(3)*	*0.020(2)*
O(32)	0.058(4)	0.062(4)	0.033(3)	0.003(3)	−0.001(3)	0.042(4)
	0.076(5)	*0.081(4)*	*0.052(3)*	*0.017(3)*	*0.007(3)*	*0.055(4)*
H						
	0.060(3)	*0.060(3)*	*0.086(10)*	*−0.011(4)*	*−0.010(3)*	*0.040(3)*

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2[h^2a^{*2}U^{11} + ... + 2hka^*b^*U^{12}]$. Parameters as determined from the X-ray data analysis are given in the first row, and those from the neutron data analysis are given in italics in the second row.

Table 7. Coordination Polyhedra in the Hexagonal Compound $Cs_2Na(HSO_4)_3$

(a) Bond Lengths (Å) in the Cesium Polyhedron and
Sodium Octahedron with Bond Multiplicities As Indicated

Cs−O(32) × 3	3.181(6)	Na−O(31)$_A$ × 6	2.393(5)
Cs−O(2) × 3	3.267(2)	Na−O(32) × 6	2.418(6)
Cs−O(1)$_D$ × 3	3.279(2)	mean	2.406
Cs−O(31)$_A$ × 3	3.513(6)		
mean	3.298		

(b) Interatomic Distances (Å) and Angles (deg) in the Sulfate Tetrahedron
with Bond Multiplicities As Indicated[a]

S	distance	angle	distance	angle	distance	angle	distance
O(2)	1.419(3)						
O(31)$_A$ × 2	1.432(5)	121.2(2)	2.484(6)				
O(32) × 2	1.479(5)	103.9(2)	2.283(6)	111.7(4)	2.408(7)		
O(1)$_D$	1.553(3)	105.4(2)	2.366(5)	112.4(2)	2.482(6)	99.7(2)	2.318(7)
		O(2)	O(2)	O(31)	O(31)	O(32)	O(32)

[a] O(31)−O(32) = 0.717(6) Å, ∠[O(31)−S−O(32)] = 28.5(2)°.

Table 8. Hydrogen Bonds in Cs−Na Acid Sulfates

compound and method	D−H···A	d(D−H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠(DHA) (deg)
CsNa₂(HSO₄)₃ X-ray	O(1)−H···O(2)	0.93(4)	1.95(5)	2.674(5)	133(5)
Cs₂Na(HSO₄)₃ X-ray	O(1)−H···O(31)	0.95(4)	1.80(4)	2.728(6)	166(6)
Cs₂Na(HSO₄)₃ neutron	O(1)−H···O(31)	1.015(9)	1.70(1)	2.708	169.8(6)

Table 9. Bond Valence Sums for the Cubic Compound $CsNa_2(HSO_4)_3$[a]

	S	Na(1)	Na(2)	Cs	H	sum
O(1)$_D$	1.15	0.13			0.96	2.24
O(2)$_A$	1.55		0.19	0.13	0.08	1.94
O(3)	1.63		0.27	0.09		1.99
O(4)	1.68	0.22		0.10		2.00
sum	6.01	1.05	1.38	0.96	1.04	

[a] Na−O and Cs−O bonds have multiplicities of three with respect to the bond sum valence at the cation site.

Table 10. Bond Valence Sums for the Hexagonal Compound $Cs_2Na(HSO_4)_3$[a]

	S	Na	Cs	H	sum
O(1)$_D$	1.21		0.10	0.91	2.22
O(2)	1.74		0.10		1.94
O(31)$_A$	1.68	0.20	0.05	0.11	1.93
O(32)	1.48	0.19	0.13		1.80
sum O(31)	6.31	1.22	0.75	1.03	
sum O(32)	5.91	1.14	0.97	0.91	
sum "O(3)"	6.11	1.18	0.86	0.95	

[a] Na−O and Cs−O bonds have multiplicities of three with respect to the bond sum valence at the cation site. The Cs−O(2) bond has a multiplicity of two with respect to the bond sum valence at the anion site.

spectively, measured in angstroms.[13] The bond valences of the O−H bonds were calculated according to

$$S(\text{H}-\text{O}) = \exp[(5.61 - d_{\text{H}-\text{O}})/0.403] \quad (4)$$

where $d_{\text{H}-\text{O}}$ is the hydrogen-to-oxygen distance, again measured in angstroms.[14] The results are presented in Tables 9 and 10, respectively, for CsNa₂(HSO₄)₃ and Cs₂-Na(HSO₄)₃. For the latter, only the results for the X-ray

(13) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244−247.
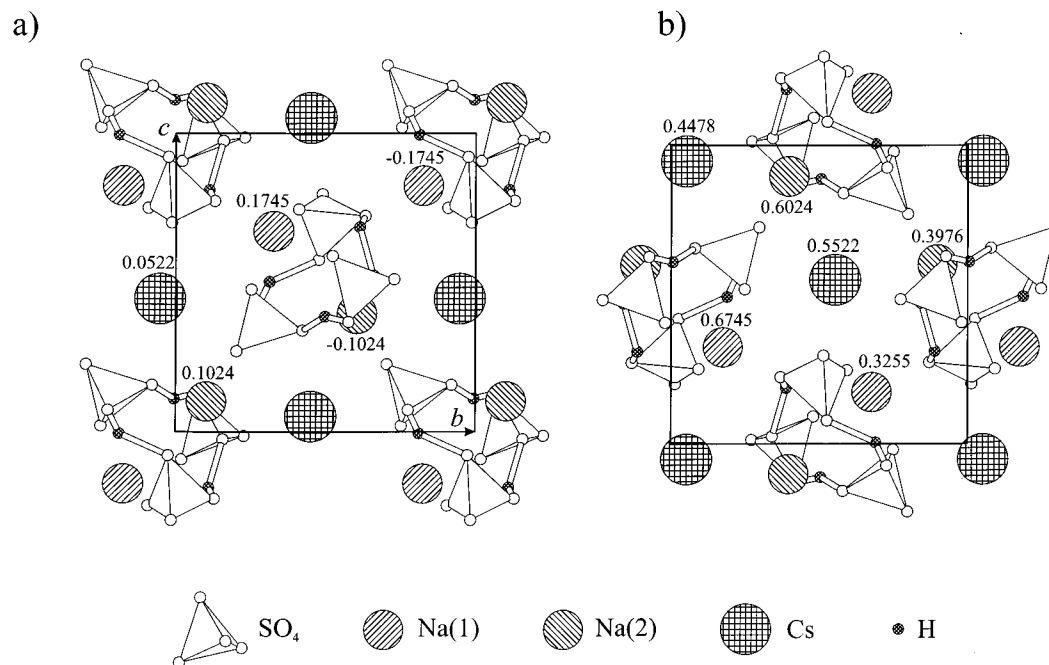(14) Alig, H.; Lösel, J.; Trömel, M. *Z. Kristallogr.* **1994**, *209*, 18−21.

structural model are provided because of the similarly between the neutron and X-ray results. The impact of the splitting of the O(3) atoms on the bond valence sums at the cation sites is noted by providing bond sums assuming three cases: (1) all such oxygen atoms reside in O(31) sites, (2) all such oxygen atoms reside in O(32) sites, and (3) such atoms are equally distributed over O(31) and O(31) sites.

In all of the above tables, oxygen atoms that serve as donors and those that serve as acceptors in the hydrogen

a)

b)

Figure 3. Structure of $CsNa_2(HSO_4)_3$ shown in projection along [100]: (a) unit cell contents from $x = -\frac{1}{4}$ to $+\frac{1}{4}$; (b) unit cell contents from $x = \frac{1}{4}$ to $\frac{3}{4}$. Elevation of alkali atoms is as indicated.

bonds are given the subscripts D and A, respectively. As is the norm, the oxygen atom that is closer to the proton is defined as the donor, and the atom further away as the acceptor, that is, $O_D-H\cdots O_A$.

Discussion of the Structures

Coordination Polyhedra. The structures of $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$ are shown in Figures 3 and 4, respectively, the former in projection along [100] and the latter along [001]. The cubic compound contains $Cs(1)O_9$ polyhedra formed by the O(2), O(3), and O(4) oxygen atoms. The O(1) atom, which serves as a donor in the hydrogen bond, does not coordinate the cesium atom. The Cs—O bond distances are rather typical, ranging from a low of 3.178(3) to a high of 3.300(4) Å, with a mean of 3.246 Å (Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751–767). The bond valence sum of 0.97 is also within the range expected.[13] There are two crystallographically distinct NaO_6 octahedra in $CsNa_2(HSO_4)_3$, both of which are centered on sites of .3. symmetry and, accordingly, are rather regular. All four oxygen atoms participate in forming these octahedra, with the Na(1)—O(1)$_D$ bond distance being the longest and the Na(2)—O(2)$_A$ the second longest of the four Na—O bonds. These results are consistent with the tendency for hydrogen bonded oxygen atoms to form weaker bonds with other cations (than non-hydrogen-bonded oxygen atoms do). An even stronger correlation between bond lengths and the role of the oxgyen atoms in hydrogen bonding is evident for the sulfate tetrahedron. Here, the difference between S—O$_D$ and S—O (where O does not participate in a hydrogen bond) is about 9%. Despite the distortion of these polyhedra, the bond valence sums at the cation sites are within experimental error of the expected values of 1 for Na(1) and 6 for S. The slightly higher bond sum valence at Na(2) is likely a simple consequence of the greater variability in bond lengths involving alkali species.[13]
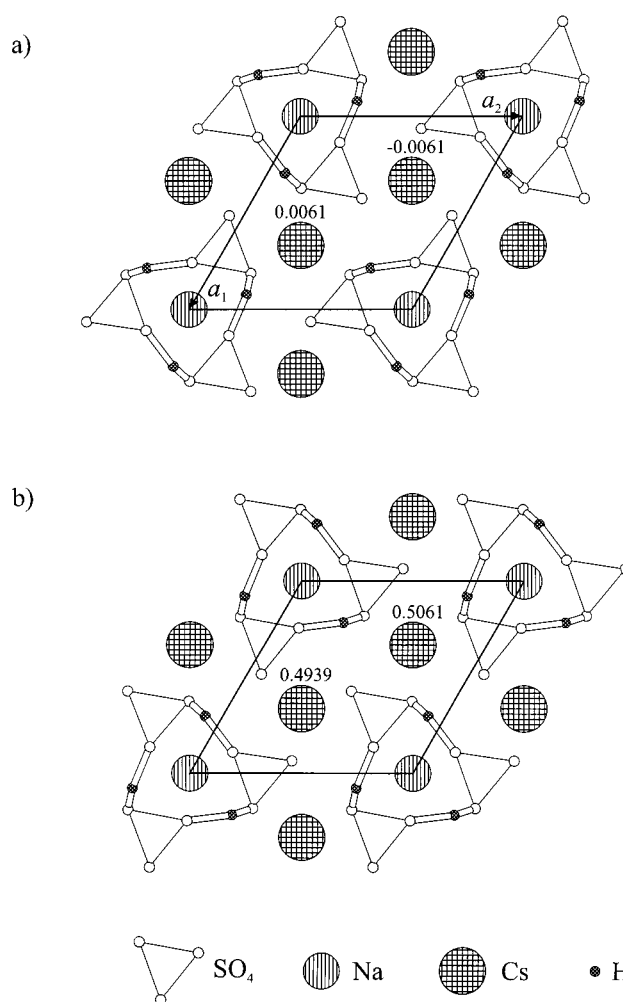
a)

b)

Figure 4. Structure of $Cs_2Na(HSO_4)_3$ shown in projection along [001]: (a) unit cell contents from $z = 0$ to $\frac{1}{2}$; (b) unit cell contents from $z = \frac{1}{2}$ to 1. Elevation of cesium atoms is as indicated. Sodium atoms are at $z = 0$ and $\frac{1}{2}$. O(32) atom sites are omitted for clarity.

The geometries of the coordination polyhedra in $Cs_2Na(HSO_4)_3$ are complicated by the presence of an oxygen atom, O(3), which (as described above) is split over two sites, O(31) and O(32). If one considers the two, $^1/_2$-occupied sites, which are separated by a distance of 0.717(6) Å, to contribute a single atom to the coordination polyhedra of each of the cations, then the Cs, Na, and S atoms in $Cs_2Na(HSO_4)_3$ have typical coordination numbers of 9, 6, and 4, respectively. The Cs—O bond distances range from 3.181 Å for O(32) (non-hydrogen-bonded) and 3.513 Å for O(31) (donor), and the sum of the bond valences is 0.86. These values are, again, quite typical, even the apparently low bond valence sum, which for large alkali cations often deviates quite significantly from 1.[13] The local position of the O(3) atom, be it in O(31) or O(32), has a fairly significant impact on the geometry of the CsO_9 polyhedron, as evident from the large difference between the Cs—O(31) and Cs—O(32) bond lengths. In contrast, the NaO_6 octahedron, formed only of O(3) atoms, is relatively insensitive to which of its possible positions O(3) occupies. The Na—O(31) and Na—O(32) bond distances are quite comparable (Table 7), as are the sums of the bond valences calculated assuming all O(31) or all O(32) coordination (Table 10).

The sulfate group in $Cs_2Na(HSO_4)_3$ is rather distorted from an ideal tetrahedron. The S—O distances range from an usually low value of 1.419 Å for O(2) and a high of 1.553 Å for O(31), the latter being a value typical for a donor oxygen atom. The intertetrahedral bond angles range from 99.7° to 121.2°, both of which deviate significantly from the ideal of 109.4°. This distortion is only in part due to the presence of a hydrogen bond which has elongated S—O_D (a similar elongation occurs in the cubic compound, but the SO_4 group is significantly more regular). It may well be that the apparent distortion is an artifact due to the disorder of the SO_4 group in $Cs_2Na(HSO_4)_3$. Specifically, the O(1) and O(2) thermal displacement ellipsoids are elongated along [001] (Table 6), suggesting that these atoms may also be displaced from the mirror plane. In such a scenario, the local positions of the O(1) and O(2) atoms may be correlated to that of the O(3) atom so as to maintain a more ideal SO_4 geometry. However, as noted above, attempts to resolve unconstrained positions for these two oxygen atoms were unsuccessful. It is noteworthy that despite the geometric distortions and disorder of the SO_4 group, the sum of the bond valences at the S atom site is nevertheless close to the expected value of 6 (assuming equal distribution of O(3) over the O(31) and O(32) sites) (Table 10).

Hydrogen Bonds. The chemical and geometric features of the hydrogen bonds in $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$ appear rather typical (Table 8). The two oxygen atoms in each bond are crystallographically independent, and accordingly, the hydrogen bond is asymmetric. The O—O distances, both ~2.7 Å, suggest that these bonds are of "medium-to-weak" strength, and according to the correlation noted by Ichikawa (1978) between O—O and O—H distances, O_D—H bond lengths on the order of 0.95 to 1.00 Å and single minimum potential wells are to be expected. In both compounds, the impact of the hydrogen bond on the sulfate group geometry, in particular the S—O_D bond distance, is

rather strong. A correlation between O_D—O_A bond lengths and S—O_D bond lengths has been noted by Catti et al.[15] and more recently refined by the present authors. Specifically, a linear regression analysis showed[16]

$$d(S-O_D) = [0.114d(O_D-O_A) + 1.256] \pm 0.12 \quad (5)$$

$$d(S-O) = [-0.028d(O_D-O_A) + 1.519] \pm 0.15 \quad (6)$$

where all distances are given in angstroms and O_D is the donor oxygen atom in a sulfate tetrahedron involved in one hydrogen bond and O represents the two oxygen atoms not forming hydrogen bonds. No correlation between S—O_A and O_D—O_A distances was evident.

The expected distances of 1.561 and 1.567 Å for the S—$O(1)_D$ bonds in $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$, respectively, based on this correlation, correspond rather well to those determined experimentally, 1.574 and 1.553 Å (Tables 4 and 7). The expected S—O distance for both compounds is 1.44 Å. Values of 1.432 and 1.444 Å are observed for $CsNa_2(HSO_4)_3$ (Table 4). In the case of $Cs_2Na(HSO_4)_3$, the observed distances, 1.419 and 1.479 (Table 7) differ significantly from the expected value and from one another. This result is reflective of the distorted and disordered nature of the SO_4 tetrahedron in the hexagonal compound.

Tetrahedral Linkage and General Structural Features. Both $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$ share a rather unusual structural feature, specifically, three-membered sulfate rings linked together via asymmetric hydrogen bonds. These rings are evident for the cubic compound in Figure 3 and for the hexagonal one in Figure 4. The stoichiometry of these compounds, in which there is one hydrogen atom per sulfate tetrahedron, immediately suggests that there should be two hydrogen bonds per SO_4 group and thus that the hydrogen bond network should be one-dimensional. In most compounds with such a H/SO_4 stoichiometry, the hydrogen bond arrangement results in infinite (HXO_4) chains, for example, $CsHSO_4$,[17] NH_4HSO_4,[18] and $RbHSO_4$,[19] or, in some cases, branched chains, for example, α-$NaHSO_4$,[20] or dimers, for example, β-$NaHSO_4$.[21] To the authors' knowledge, no other ring-based structures have been previously observed.

The $(HSO_4)_3$ rings in $CsNa_2(HSO_4)_3$ form a cubic close-packed array and alternate with the Cs atoms (Figure 3) in a manner similar to that for the sodium chloride structure. Each of the rings lies in a plane parallel to {111}. This is evident in Figure 5, a projection along [111] of the $(HSO_4)_3$ group centered about the unit cell origin. The thermal ellipsoid representation (Figure 4b) reveals that the thermal displacements of the oxygen

(15) Catti, M.; Ferraris. G.; Ivaldi, G. *Acta Crystallogr.* **1979**, *B35*, 525−529.
(16) Haile, S. M.; Calkins, P. M. *J. Solid State Chem.* **1998**, *140*, 251−265. Notes: Due to a typographical error, the numerical values given for the correlations relating S−O and O−O bond distances in Haile and Calkins (1998) are in error. The graphical data, however, are presented correctly.
(17) Chisholm, C. R. I.; Haile, S. M. *Mater. Res. Bull.* **2000**, *35*, 999−1005.
(18) Nelmes, R. J. *Acta Crystallogr.* **1971**, *B27*, 272−281.
(19) Ashmore, J. P.; Petch, H. E. *Can. J. Phys.* **1975**, *53*, 2694−2702.
(20) Sonneveld, E. J.; Visser, J. W. *Acta Crystallogr.* **1979**, *B35*, 1975−1977.
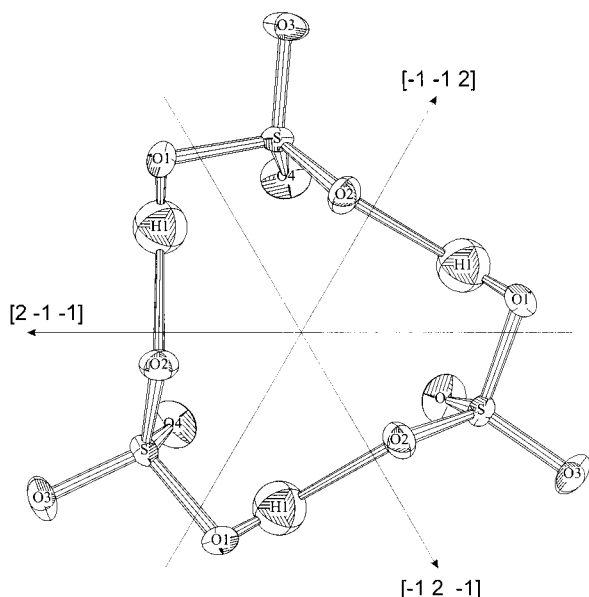(21) Sonneveld, E. J.; Visser, J. W. *Acta Crystallogr.* **1978**, *B34*, 643−645.

Figure 5. Projection along [111] of the structure of the $(HSO_4)_3$ rings in $CsNa_2(HSO_4)_3$ shown in a thermal ellipsoid representation (electron probability of 50%). The ring center is located at approximately $-0.07, -0.07, -0.07$.

atoms are oriented primarily along a direction perpendicular to the S−O bond, as is expected. The Na atoms of $CsNa_2(HSO_4)_3$ are located within what can be regarded as the tetrahedral sites of the cubic close-packed $(HSO_4)_3$ array and serve to link together four $(HSO_4)_3$ rings. Overall, the structure can then be understood as a derivative of the Cu_2MnAl Heussler alloy structure-type.[22] The cation polyhedra in $CsNa_2(HSO_4)_3$ are fairly isolated from one another. The CsO_9 polyhedron shares each of its three $O(2)−O(3)$ edges with a $Na(2)O_6$ octahedral edge, and each of its three $O(4)$ corners with a $Na(1)O_6$ octahedral corner. The sulfate tetrahedra share corners with the CsO_9 and NaO_6 polyhedra (consistent with the coordination polyhedra defined in Table 4). No other direct polyhedral linkages are formed. The linkage between the sodium octahedra and the $(HSO_4)_3$ rings has a rather special configuration. As shown in Figure 6, which depicts a portion of the structure about the origin, one of the octahedral faces in both $Na(1)O_6$ and $Na(2)O_6$ is formed by three oxygen atoms of the same $(HSO_4)_3$ ring. The remaining three oxygen atoms derive from distinct $(HSO_4)_3$ rings, producing the pseudotetrahedral coordination of Na by $(HSO_4)_3$ groups described above.

In the hexagonal compound $Cs_2Na(HSO_4)_3$, the $(HSO_4)_3$ rings are arranged in a pseudosimple hexagonal array (Figure 4) with an array repeat distance along c that is $^1/_2$ the unit cell length. The thermal ellipsoid representation of a portion of one of the rings (Figure 7) reveals the nature of the local structural disorder about the SO_4 group geometry alluded to earlier. It appears that the hydrogen bond between $O(1)$ and $O(3)$ causes the sulfate group to deviate locally from the symmetry implied by the mirror plane at $z = ^1/_4$. Specifically, as a hydrogen bond is formed between $O(1)$ and one of the $O(3)$ atoms, the latter is pulled into the $O(31)$ position and the remaining $O(3)$ atom pushed into the $O(32')$ position.
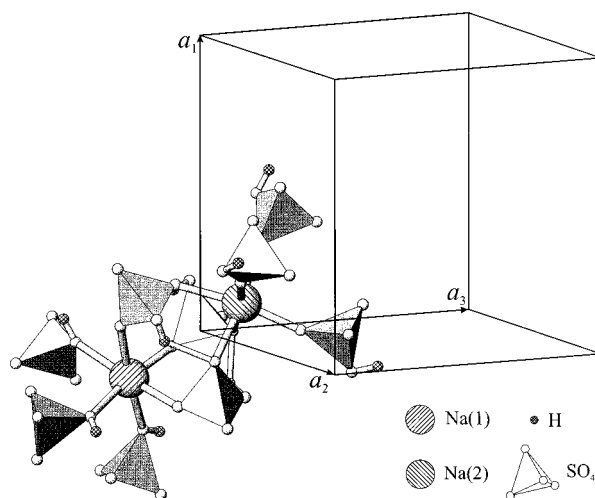
(22) Soltys, J. *Phys. Status Solidi A* **1981**, *66A*, 485−491.

Figure 6. Portion of the structure of $CsNa_2(HSO_4)_3$ about the origin showing coordination between Na and $(HSO_4)_3$ rings.
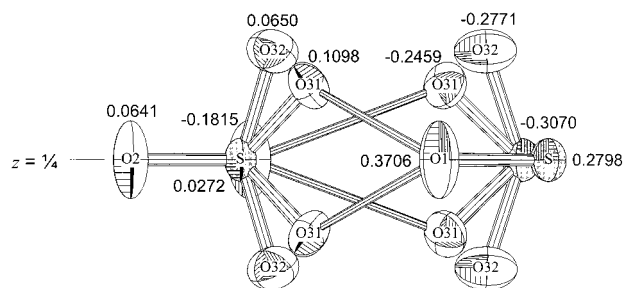

Figure 7. Projection on (011) of a portion of the $(HSO_4)_3$ ring in $Cs_2Na(HSO_4)_3$ shown in a thermal ellipsoid representation (electron probability of 50%). Elevation of atoms is as indicated. Protons are omitted for clarity.

The refinement of the structural data indicates (by the better fit of the $P6_3/m$ model than the $P6_3$ model to the diffraction data) that neither of the two possible orientations of the SO_4 group is preferred globally over the other. That is, the orientation from one sulfate group to the next, and perhaps even for a single sulfate group from one instant to the next, varies and does so in either a dynamic and/or static manner.

As with the cubic compound, the NaO_6 octahedra in the structure of $Cs_2Na(HSO_4)_3$ serve to link the $(HSO_4)_3$ rings to one another. In this case, however, rather than a three-dimensional $Na_2(HSO_4)_3$ framework, one-dimensional $Na(HSO_4)_3$ chains which extend along [001] are formed, as can be surmised from examination of Figure 3. Unlike the case of the cubic compound, both the upper and lower faces of the NaO_6 octahedron are formed by three oxygen atoms of the same $(HSO_4)_3$ ring. Linkages between the $Na(HSO_4)_3$ chains are formed via the CsO_9 polyhedra. This latter group shares each of its three $O(3)−O(1)$ edges and $O(2)$ corners with distinct sulfate tetrahedra, so as to link together three $Na(HSO_4)_3$ chains.

Concluding Remarks

The compounds $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$ share a crystal-chemical feature, the presence of three-membered sulfate rings, that is unique among acid sulfates. In both of these compounds sodium octahedra share one if not two polyedral faces directly with one of

these rings. The geometric "match" between these two structural components [$(HSO_4)_3$ rings and NaO_6 octahedra] suggests that sodium ion polyhedra may serve to template the hydrogen bond network and sulfate group connectivity. Such a proposition would be supported by the discovery of an $NaHSO_4$ polymorph that contains similar three-membered $(HSO_4)_3$ rings.

Supporting Information Available: Tables of observed and calculated structure factors for $Na_2Cs(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$ (4 pages PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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