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Structure refinement and chemical analysis of $Cs_3Li(DSO_4)_4$, formerly '$Cs_{1.5}Li_{1.5}D(SO_4)_2$'

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Abstract

An accurate structure refinement of the deuterated analog of the cesium lithium acid sulfate, formerly identified as '$Cs_{1.5}Li_{1.5}H(SO_4)_2$', has been carried out using neutron diffraction methods. Like the protonated material reported earlier (Merinov et al., Solid State Ionics 69 (1994) 53), the compound is cubic, $I\bar{4}3d$, however, the correct stoichiometry is $Cs_3Li(DSO_4)_4$. There are four formula units per unit cell and six atoms in the asymmetric unit. The lattice constant measured in this work is $a = 11.743(2)$ Å, comparable to the earlier results. The structure contains one disordered hydrogen bond, formed between O(2) atoms and located on two of the edges of the single LiO_4 tetrahedron. The Li site occupancy is $\frac{1}{3}$, as is that of the deuterium site. This level of site occupancies is consistent with a structure in which hydrogen bonds are formed only when the lithium site is unoccupied, and explains the otherwise close proximity of the Li and D atoms, 1.394(10) Å. This unusual structural feature furthermore leads to a fixed stoichiometry, as confirmed here by chemical analysis of both the deuterated and protonated materials, despite the partial occupancy of the lithium and deuterium (hydrogen) atom sites.

Keywords: Inorganic compounds; Neutron diffraction; Crystal structure; Ionic conductivity; Proton conductivity; $CsHSO_4$

1. Introduction

The proton transport properties of the compound '$Cs_{1.5}Li_{1.5}H(SO_4)_2$' have attracted some interest because of its high symmetry at ambient temperatures, and apparently unusual hydrogen bond network [1–3]. Specifically, the compound crystallizes in space group $I\bar{4}3d$ and is reported to possess hydrogen-bonded chains of SO_4 groups, in which the average bond occupancy by protons is $\frac{1}{6}$. Any understanding of the proton transport mechanisms requires a complete and accurate assessment of the proton sites within the structure, however, this is generally not possible by X-ray diffraction as was the basis of the earlier study. Indeed, ambiguities about the proton positions in this compound have been noted [2]. The present neutron diffraction study was carried out in order to unequivocally determine the location of protons/deuterons within the structure.

2. Synthesis and chemical analysis

Colorless, transparent single crystals were grown by slow evaporation at room temperature from aqueous solutions of $Cs_2CO_3/Li_2CO_3/D_2SO_4$ in a molar ratio of 4:1:16 in D_2O [2]. The protonated material was obtained analogously. The identity of crystals used for further experimentation was confirmed by single-crystal X-ray methods (Scintex 4-circle goniometer). Crystals of the desired phase were also recognizable from their tetrahedral habit.

Preliminary analysis of the neutron diffraction data suggested that the composition of the Cs–Li acid sulfate differed from that reported earlier, prompting chemical analysis. Measurement of the Cs and Li concentrations in the crystals was performed by ICP-MS (inductively coupled plasma mass spectrometry; Hewlett Packard 4500). A single crystal (100 mg) was dissolved into 1% HNO_3 (100 mL), which was further diluted to a concentration of less than 0.1 ppm by mass of Li and Cs. This solution was introduced into the ICP-MS and the resultant Cs and Li signals ($m/z = 133$ and 7,

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respectively) converted into concentration using previously determined calibration scales. Four separate solutions (using different single crystals) were prepared for both the deuterated and protonated compounds, and each solution measured ten times. The calibration scales were determined by dilution (to several different levels) of standard solutions of Li and Cs in 1% HNO_3. Measurements of the standard solutions were also performed ten times each. Using these methods the Cs and Li mass percentages were found to be 50% (±5%) and 0.79% (±0.04%), respectively, for the deuterated compound and 51.1% (±0.6%) and 0.895% (±0.011%) for the protonated. These values imply molar ratios of Cs/Li of 3.3 (±0.3) and 2.98 (±0.04), respectively, for the two materials.

An estimate of the level of deuteration for the sample prepared in heavy water was performed by ^1H MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy, as described elsewhere [2]. Those results indicated deuteration of at least 50% in powdered samples, suggesting that single-crystal samples, with much lower specific surface area over which D → H exchange can occur, would have significantly greater deuterium concentrations.

3. Single-crystal neutron diffraction

3.1. Experimental

A crystal of the deuterated cesium lithium sulfate was mounted on an aluminum pin for neutron diffraction experiments using epoxy glue. The diffraction data were obtained at room temperature on the four-circle diffractometer 2TanA at the High Flux Isotope Reactor at the Australian Nuclear Science and Technology Organisation (ANSTO). The neutron beam, monochromated by copper (220), had a wavelength of 1.235(1) Å. From $\sin 2\theta$ values of 19 reflections ($14° < 2\theta < 60°$), the unit-cell constant of the title compound, with cubic space group $I\bar{4}3d$, was determined to be $a = 11.734(2)$ Å, giving a cell volume of $V = 1615.6(8)$ Å^3.

Reflections were collected using the ANSTO program DIFF and were scanned for a half sphere of reciprocal space, using $\theta/2\theta$ step scans. In the data collection, counts were accumulated at each step for a preset monitor count of the incident beam. Intensities of three reflections were monitored approximately every 40 reflections as a check on experimental stability, which proved to be excellent throughout the 4 days of data collection. Altogether, 972 reflections were scanned, including standards. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles using the ANSTO software DIFFPLOT and PLT2HKL. Lorentz factors were applied. No absorption correction was applied.

Averaging over symmetry-related reflections gave an internal agreement factor on F_o^2 of 0.0226. After removing the systematic absences, this resulted in 125 independent observations, of which 122 had F_o^2 values $> 3\sigma(F_o^2)$.

3.2. Results

The structure refinement was based on all independent F_o^2 values using the program UPALS [4]. The atomic positions from the X-ray study of '$Cs_{1.5}Li_{1.5}H(SO_4)_2$' [1], including those of the hydrogen/deuterium atom, were used as the starting structure. It soon became apparent that the deuterium atom position was in error, and that the Li site occupancy was significantly lower than one. A Fourier difference map was used to identify the appropriate deuterium site, and occupancies of both this atom and the Li atom were varied. The Li atom site occupancy refined to a chemically meaningful (described below) value of $\sim\frac{1}{3}$, implying, for reasons of overall charge balance, a site occupancy at the deuterium position of also $\frac{1}{3}$. This diffraction result motivated the chemical analysis reported above, which also indicated a much lower Li content than reported in the X-ray study. Fixing the Li occupancy at $\frac{1}{3}$ and allowing for partial occupation of the deuterium site by hydrogen yielded a D:H ratio of 85:15, a physically plausible value in light of the NMR studies [2]. The resulting stoichiometry of $Cs_3Li(D_{0.85}H_{0.15}SO_4)_4$ implies Cs and Li mass percentages of 50.01 and 0.87, respectively, in good agreement with the chemical analysis. Accordingly, the Li occupancy was fixed at $\frac{1}{3}$ for subsequent refinements, and those of the D and H atoms at 0.283, and 0.05, respectively, by using a scattering factor at the D atom site that reflected the mixed D and H occupancy and applying an overall occupancy factor of $\frac{1}{3}$.

In the final refinement cycle, the scale factor was varied, together with the positional and symmetry allowed anisotropic displacement parameters for all 6 atoms comprising the molecule in the asymmetric unit, for a total of 29 variables. No extinction correction was applied. Using this model, after convergence was achieved with $\Delta p/\sigma(p) < 0.1$, final agreement factors were obtained as follows: $R(F_o^2) = 0.0504$, $wR(F_o^2) = 0.0495$, $S = 1.034$ with weights $w^{-1} = (\sigma^2 + [0.01\ F_o^2] + 3)^2$. Conventional agreement factors for the 122 reflections with $I > 3\sigma(I)$ are $R(F_o) = 0.0343$ and $wR(F_o) = 0.0360$. Scattering lengths were taken from the literature [5]. The crystallographic data and refinement statistics are summarized in Table 1. Atomic positional and anisotropic displacement parameters are listed in Tables 2 and 3, respectively. For comparison, atomic coordinates and isotropic displacement parameters of the X-ray study are also given in Table 2. The final difference Fourier map showed no residual positive

Table 1
Crystal data, data collection parameters and final refinement conditions for $Cs_3Li(DSO_4)_4$

Empirical formula	$Cs_3Li_1D_4S_4O_{16}$
Formula weight	398.97
Temperature	300 K
Wavelength	1.235 Å
Crystal system	Cubic
Space group	$I\bar{4}3d$
Unit cell dimensions	$a = 11.734(2)$ Å
Volume	1615.6(8) $Å^3$
Z	4
Density (calculated)	3.280 Mg/m^3
Absorption coefficient	0.229 mm^{-1}
$F(000)$	581.1680 fm
Crystal size	$4.2 \times 4.2 \times 4.2\,mm^3$
θ range for data collection	7–45°
Index ranges	$-13 \leqslant h \leqslant 8$, $-9 \leqslant k \leqslant 9$, $-13 \leqslant l \leqslant 13$
Reflections collected	972
Independent reflections	125[R(int) = 0.0226]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	125/0/29
Goodness-of-fit on F^2	1.034
Final R indices (all data) on F^2	$R_2 = 0.0504$, w$R_2 = 0.0495$
Conventional R indices ($I > 3\sigma(I)$, on F)	$R_1 = 0.0343$, w$R_1 = 0.0360$
Weighting scheme	$w^{-1} = (\sigma^2 + [0.01F_o^2] + 3)^2$
Largest difference peak and hole	1.1% and 1.0% of maximum (Cs)

Table 2
Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $Cs_3Li(DSO_4)_4$

	Site	x	y	z	$U_{(eq)}$
S	16*c*	0.3367(4)	0.3367(4)	0.3367(4)	0.018(2)
		0.3368(1)	*0.3368(1)*	*0.3368(1)*	*0.0222(3)*
O(1)	16*c*	0.4068(2)	0.4068(2)	0.4068(2)	0.045(2)
		0.4076(2)	*0.4076(2)*	*0.4076(2)*	*0.0499(3)*
O(2)	48*e*	0.3953(4)	0.3043(3)	0.2299(2)	0.037(2)
		0.3961(2)	*0.3036(2)*	*0.2296(2)*	*0.0417(11)*
Cs	12*a*	0	1/4	3/8	0.029(2)
					0.0306(1)
Li[a]	12*b*	1/2	1/4	1/8	0.016(9)
					0.15(3)
D[b]	48*e*	0.4699(10)	0.2653(11)	0.2389(8)	0.037(8)
'H-bond'		*0.4806*	*0.5269*	*0.4436*	*n/a*

$U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U^{ij} tensor. Values in italics are those reported earlier based on an X-ray study [1].

[a] Site occupancy of $\frac{1}{3}$ [fixed during final stages of refinement].

[b] Overall site occupancy of $\frac{1}{3}$, occupied by 85% D/15% H [fixed during final stages of refinement].

and negative peaks with significant scattering density; the maximum difference peak was about 1.1% of the scattering density at the cesium atom peak.

Table 3
Anisotropic displacement parameters ($Å^2$) for $Cs_3Li(DSO_4)_4$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S	0.018(1)	0.018(1)	0.018(1)	0.004(2)	0.004(2)	0.004(2)
O(1)	0.045(1)	0.045(1)	0.045(1)	−0.011(1)	−0.011(1)	−0.011(1)
O(2)	0.039(2)	0.042(2)	0.031(2)	−0.003(1)	0.012(1)	0.008(1)
Cs	0.028(2)	0.028(2)	0.030(4)	0	0	0
Li	0.012(11)	0.012(11)	0.025(20)	0	0	0
D	0.040(11)	0.032(7)	0.038(5)	0.001(5)	0.003(5)	0.003(7)

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

Selected portions of the overall structure are shown in projection on (111) in Fig. 1, and a thermal ellipsoid representation is presented in Fig. 2.

4. Discussion: structure and stoichiometry

The lattice parameter and the atomic coordinates of the heavy atoms obtained in this work are in general agreement with those reported for $Cs_{1.5}Li_{1.5}H(SO_4)_2$ and determined by single-crystal X-ray studies [1], Table 2. The overall structural features of this compound have been described in Ref. [1], and are discussed only briefly here. Eight oxygen atoms coordinate the single, crystallographically distinct cesium atom with Cs–O bond distances of less than 3.35 Å, whereas both the lithium and sulfur atoms are tetrahedrally coordinated, Fig. 1. The single, crystallographically distinct SO_4 tetrahedron is rather regular. The S–O(1) bond is 1.423(5) Å in length, whereas the three S–O(2) bonds are 1.479(5) Å. The O–S–O angles differ from perfect tetrahedral values by less than 3°, and the O–O ligand distances are within 0.02 Å of one another, Table 4. In contrast, the LiO_4 tetrahedron, formed entirely of O(2) oxygen atoms, is highly distorted, with one pair of O(2)–O(2) ligand distances measuring 2.767(8) Å, and the other four 3.164(5) Å. The thermal displacements of the oxygen atoms are generally perpendicular to the S–O and Li–O bonds, as would be expected, whereas the S and Cs atoms exhibit almost isotropic displacements, Fig. 2. The thermal ellipsoid of the Li atom is markedly more anisotropic, with its greatest displacement parallel to the direction of elongation of the tetrahedra within which it resides (Table 5).

In the X-ray structure refinement [1], the Li site was assumed to be fully occupied, and, because of the weak X-ray scattering power of Li, the model reached convergence with good refinement statistics. It is noteworthy, however, that the thermal displacement parameter obtained for Li in that work was unusually high [$U_{eq} = 0.15\,Å^2$] suggesting that that crystal had a similar partial occupancy on the Li site. An analysis of the O–O distances between sulfate groups led the authors to conclude that protons resided on a general

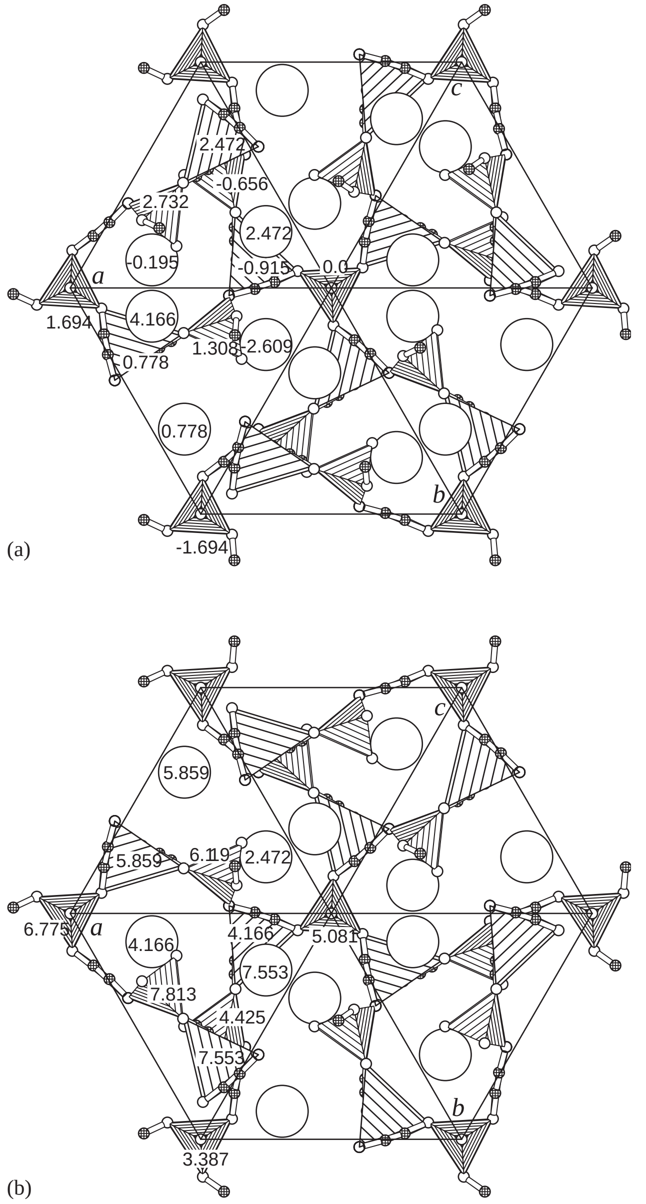

Fig. 1. The structure of $Cs_3Li(DSO_4)_4$ shown in projection on (111); (a) structure from ~ (−0.05, −0.05, −0.05) to (0.32, 0.32, 0.32) and (b) from ~ (0.2, 0.2, 0.2) to (0.54, 0.54, 0.54). Only complete tetrahedra are shown. Those with large spacing between shading lines are LiO_4 groups and the remainder SO_4 groups. Numbers on Cs atoms and tetrahedral groups correspond to Cs, Li and S atom elevations in Å relative to the central S atom in (a) at 0.0867, 0.0867, 0.0867. The apparent proximity of the Li and D atoms is accounted for by the partial occupancies, as discussed in the text.

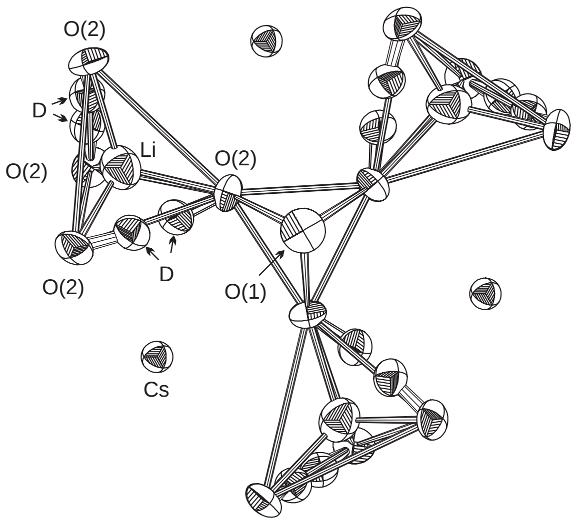

Fig. 2. Thermal ellipsoid representation of the structure of $Cs_3Li(DSO_4)_4$, shown in projection on (111). Portion of the structure depicted corresponds to the center of Fig. 1(a).

Table 4
Interatomic distances (Å) and bond angles (deg) in the coordination polyhedra in $Cs_3Li(DSO_4)_4$

Cs coordination polyhedron		
Cs–O(2) [4 ×]	3.298(3)	
Cs–O(1) [4 ×]	3.337(2)	
SO_4 tetrahedron	This work	X-ray study [1]
S–O(1)	1.425(5)	1.433(2)
S–O(2) [3 ×]	1.479(5)	1.484(2)
O(1)–O(2) [3 ×]	2.402(4)	
O(2)–O(2) [3 ×]	2.381(6)	
O(1)–S–O(2) [3 ×]	111.6(3)	
O(2)–S–O(2) [3 ×]	107.2(3)	
LiO_4 tetrahedron	This work	X-ray study [1]
Li–O(2) [4 ×]	1.852(3)	1.834(2)
O(2)–O(2) [2 ×]	2.767(8)	2.734(3)
O(2)–O(2) [4 ×]	3.164(5)	3.118(3)
O(2)–Li–O(2) [2 ×]	96.7(2)	
O(2)–Li–O(2) [4 ×]	116.2(1)	
O(1)–O(2)	3.401(5)	3.376(3)

The oxygen–oxygen distance (Å) between neighboring but isolated SO_4 tetrahedra (not linked via either hydrogen bonds or LiO_4 tetrahedra) is also given. Interatomic distances are compared to those obtained for '$Cs_{1.5}Li_{1.5}H(SO_4)_2$' [1].

position between O(1) and O(2) [$d_{O-O} = 3.376(3)$ Å in the X-ray analysis and 3.401(5) Å in the present neutron study], far from the lithium ion and linking sulfate groups along the body diagonals of the cubic unit cell. For overall charge balance, the hydrogen bond occupancy was assumed to be $\frac{1}{6}$. In the present work, the deuterium ion position was directly located by Fourier difference maps, and because of the large scattering length of D, there is no ambiguity in its position. It was found to reside on the contracted edge of the LiO_4 tetrahedron, providing an explanation for the severe distortion of this tetrahedral group. This positioning, together with the occupancies obtained for the Li and D site, can be interpreted as follows. Of the possible LiO_4 tetrahedra, only $\frac{1}{3}$ are filled with Li atoms. When the Li ion site is filled, the possible hydrogen bonds at its two edges are unoccupied. In the remaining $\frac{2}{3}$ of cases, both hydrogen bonds are occupied, with deuterium ions residing in double minimum potential wells such that the

Table 5
Interatomic distances (Å) and angles (deg) in the hydrogen bond of $Cs_3Li(DSO_4)_4$

$O_{A/D}$–$D_{1/2}$–$D_{1/2}$–$O_{A/D}$	$d(O_D–D)$	$d(D\cdots O_A)$	$d(O_D\cdots O_A)$	$<(O_D\ D\ O_A)$	$<(S\ O_D\ D)$		
O(2)–D···O(2)	0.993(12)	1.784(12)	2.767(8)	170.6(9)	116.0(6)		
D–D	0.79(2)	Li–D	1.394(10)	Cs–D	3.304(12)	Cs–D	3.309(13)

Distances (Å) between the deuterium atom site and selected cations are also given.

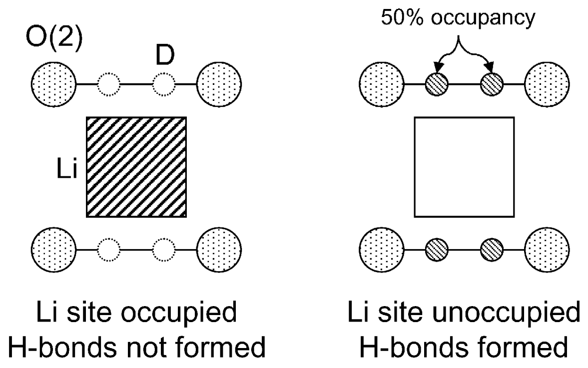

Fig. 3. Schematic representation of the structure in the region of the hydrogen bond and lithium atom site. The configuration on the left, in which the Li site is occupied and the hydrogen bonds on the edges of the tetrahedra are unoccupied, occurs for $\frac{1}{3}$ of the tetrahedra, whereas the configuration on the right, in which the hydrogen bonds are occupied and the Li site is unoccupied, occurs for the remaining $\frac{2}{3}$ of the tetrahedra.

deuterium ion site occupancy is lowered by a factor of 2 to $\frac{1}{3}$. The situation is illustrated in Fig. 3. The fact that the thermal displacement parameters of O(2) are not enhanced relative to the other atoms in the structure suggests that the local bonding configuration, and in particular the position of O(2), is equally well suited to both the LiO_4 tetrahedron and the hydrogen bond.

The hydrogen bond in $Cs_3Li(DSO_4)_4$ is formed between O(2) atoms related by a two-fold axis of rotation and separated by a distance of 2.767(8) Å. As such, the bond can be classified as a symmetric bond with 'medium-to-weak' strength. Within this bond, the deuterium ion resides in a double minimum potential well and the oxygen atoms have mixed donor/acceptor character. According to the analysis of Ichikawa [6], who has examined the structural features of hydrogen bonds in a broad range of inorganic compounds, such a combination of bond strength and symmetry is unusual, and a single-minimum, asymmetric bond is expected for hydrogen bonds greater than ~2.6 Å in length. The present result is likely a consequence of the partial occupancy at the deuterium ion site, which produces, on average, O–O distances that are longer than the case of a fully occupied site. The remaining structural features of the hydrogen bond are rather typical. The distance between the donor oxygen atom, O_D, and the deuterium ion is 0.993(12) Å, falling within error of the correlation curve between O_D–H and O···O distances noted by Ichikawa. Similarly, Brown [7] has summarized the correlation between the acceptor oxygen, O_A, to hydrogen distance and the O_D–H–O_A angle, and again, the parameters of the hydrogen bond found here, 1.784(12) Å and 170.6(9)°, respectively, fall well within the scatter of that correlation curve. The fact that a rather linear bond is obtained here, moreover, is consistent with a hydrogen bond that is of higher strength than immediately suggested by the average O(2)–O(2) distance of 2.767(8) Å. The hydrogen bonding at the O(2) atom has the rather usual effect of elongating the S–O(2) bond relative to the S–O(1) bond [8], in this case by an amount of 0.054 Å.

The disorder and partial occupancies in $Cs_3Li(DSO_4)_4$ have, surprisingly, the final effect of imposing a fixed stoichiometry on the compound. This can be understood by examining the extreme case of a fully occupied Li site. In such a case, two deuterium ions per formula unit are required for overall charge balance [i.e., $Cs_3Li_3D_2(SO_4)_4$]. Introducing them at the O(2)–O(2) hydrogen bond would, however, lead to overbonded O(2) atoms because these oxygen atoms would already be adequately bonded to Li. Similarly, the maximum deuterium occupancy that could be accommodated by the overall stoichiometry is $\frac{5}{12}$ [i.e., $Cs_3D_5(SO_4)_4$]. In this case, only some of the hydrogen bonds would be occupied, while there would be no lithium ions, resulting in underbonded O(2) atoms. In order to provide the ideal bonding for O(2) atoms, such that, in addition to bonding to sulfur, they either participate in hydrogen bonds or in the formation of LiO_4 tetrahedra (never both and never neither) the exact stoichiometry of $Cs_3Li(DSO_4)_4$ is necessary.

The fixed stoichiometry of $Cs_3Li(DSO_4)_4$ suggests (but by no means requires) that, locally, each SO_4 group shares a corner with only one LiO_4 tetrahedron via one of the three O(2) atoms, while the remaining two O(2) atoms form hydrogen bonds. Such a scenario furthermore raises the possibility of an ordered arrangement of Li and D atoms. Although signs of long range ordering of Li and D atoms were not explicitly sought out in this work, such behavior would likely be rather obvious in a neutron diffraction experiment given the magnitude of the scattering factors of these two elements. Ordering would also be anticipated to introduce additional changes in the structure that would break the apparent cubic symmetry in a manner detectable even by X-ray diffraction. This latter situation is observed in α-$Cs_3(H_2PO_4)(HSO_4)$, in which ordering of the PO_4 and

SO_4 groups leads to a superstructure relative to $CsHSO_4$ which is easily observable by X-ray diffraction, despite the almost identical X-ray scattering factors of S^{6+} and P^{5+} [9]. These types of global changes would also diminish the possibility that ordering has been masked by the examination of a twinned crystal.

Despite the fact that long range ordering is unlikely to have been overlooked, it is nevertheless instructive to consider what kind of locally ordered arrangement could be accommodated by the macroscopic cubic symmetry of $Cs_3Li(DSO_4)_4$. Such an exercise is particularly valuable because a low temperature phase transition has been reported for this compound, occurring at 162 K for the protonated material and 153 K for the deuterated [3], and allows one to postulate the low temperature structure. Ordering of the Li atoms could lead either to a tripling of one of the axes or a reduction in symmetry without a substantial change to the cell dimensions. Of these, the latter appears more relevant, in that the space group $I\bar{4}2d$ is a maximal subgroup of $I\bar{4}3d$ and provides exactly the increase by a factor of three of the asymmetric unit implied by the $\frac{1}{3}$ occupancy of the Li site.

Plausible atomic coordinates for an ordered arrangement in space group are given in Table 6; here, a shift in origin by (0, $\frac{1}{4}$, $\frac{7}{8}$) upon transforming from the cubic to tetragonal cell has been applied. Immediately evident is that the Li 12*b* site of the cubic cell splits into one 4*b* site and one 8*d* site in the tetragonal cell. The latter must be unoccupied to reflect the experimentally determined stoichiometry. In terms of Fig. 1, the three-fold axis along [111] is removed, and only one of the three LiO_4 tetrahedra surrounding the central SO_4 group remains. Like the lithium atom, the Cs 12*a* site also splits into two, but in this case both sites remain occupied. As alluded to above, long range ordering of Cs atoms in this manner (with the *y* coordinate of Cs(1) shifting away from 0.875) would easily be detectable by either X-ray or neutron diffraction. The O(2) and D atoms, both residing at general 48*e* positions in the cubic cell, each reside in three distinct 16*e* sites in the tetragonal cell, O(21), O(22) and O(23), and D(1), D(2) and D(3), respectively. One of the D atom sites, D(1), is in close proximity to the occupied Li site, and can be taken to be unoccupied. Thus, the O(21) oxygen atoms form the

Table 6
Atomic coordinates of the proposed low-temperature, tetragonal structure of $Cs_3Li(DSO_4)_4$ in which Li and D atoms are ordered

$I\bar{4}3d$				Site	Occ	$I\bar{4}2d$		
	Site	Occ				*x*	*y*	*z*
S	16*c*	1	S	16*e*	1	0.3367	0.5867	0.2117
O(1)	16*c*	1	O(1)	16*e*	1	0.4068	0.6568	0.2818
O(2)	48*e*	1	O(21)	16*e*	1	0.3953	0.5543	0.1049
			O(22)	16*e*	1	0.8547	0.7299	0.3207
			O(23)	16*e*	1	0.5201	0.1957	0.5203
Cs	12*a*	1	Cs(1)	8*d*	1	1/4	0.875	3/8
			Cs(2)	4*a*	1	0	0	0
Li	12*b*	1/3	Li(1)	4*b*	1	0	0	1/2
			Li(2)	8*d*	0	0.8750	1/4	1/8
D	48*e*	1/3	D(1)	16*e*	0	0.4699	0.5153	0.1139
			D(2)	16*e*	1/2	0.7801	0.7389	0.3597
			D(3)	16*e*	1/2	0.5111	0.2347	0.5949

A comparison with the atomic sites in the cubic structure is provided. The resultant Li(2) and D(1) sites of the tetragonal modification are presumed unoccupied in accordance with the material stoichiometry.

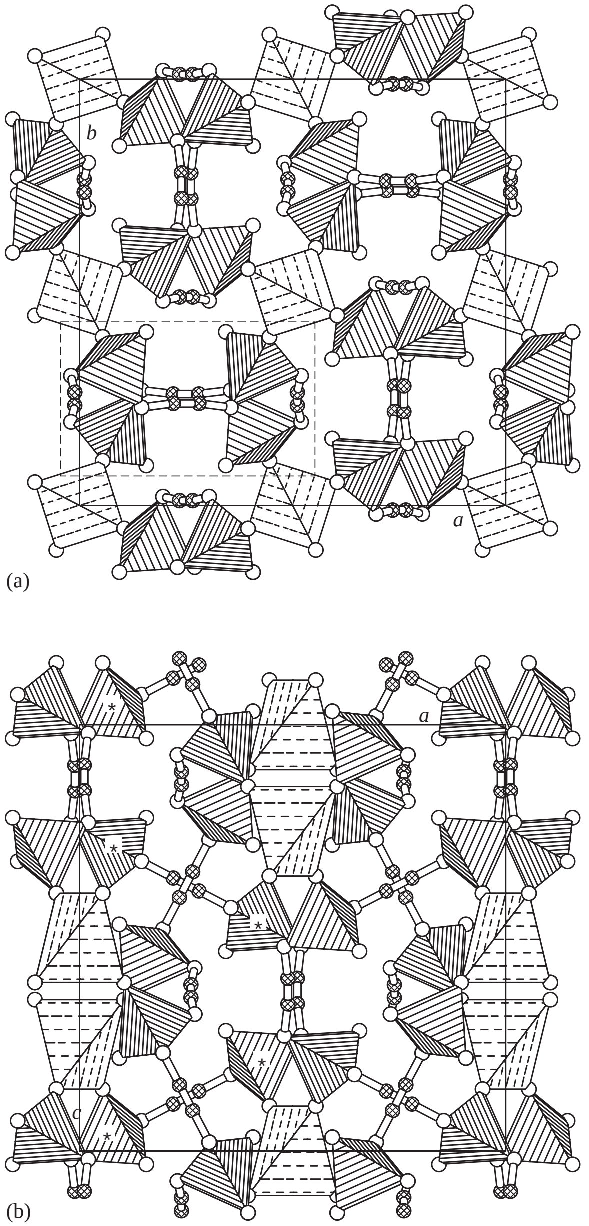

Fig. 4. Hypothesized structure of $Cs_3Li(DSO_4)_4$ with an ordered arrangement of Li and D atoms, space group $I\bar{4}2d$; shown in projection (a) on (001) and (b) on (010). Cs atoms omitted for clarity. Tetrahedra with hatched lines correspond to LiO_4 groups and the remainder to SO_4 groups. In (a) a single $(HSO_4)_\infty$ chain extending parallel to [001] is outlined. The corresponding SO_4 tetrahedra are indicated with an asterisk in (b).

LiO_4 tetrahedra, whereas the O(22) and O(23) atoms form crystallographically distinct hydrogen bonds about D(2) and D(3), respectively. If the symmetry of the ordered arrangement is not reduced further from $I\bar{4}2d$, these two hydrogen bonds are macroscopically symmetric, with the donor and acceptor oxygen atoms related by a two-fold axis of rotation, as they are in the $I\bar{4}3d$ cubic arrangement.

Projections of the proposed tetragonal structure along (001) and (010) are presented in Fig. 4. The SO_4 groups are linked by hydrogen bonds to form a 'square-tooth' $(DSO_4)_\infty$ chain extending along c. Four such chains are contained within each unit cell and they are linked to one another via LiO_4 tetrahedra, with each corner of any LiO_4 group connected to a different chain. The cubic structure can be interpreted as a three-fold superposition of this tetragonal arrangement, with sulfate chains extending along all three axes, but with randomly missing hydrogen bonds. Overall, the SO_4 and '$Li_{1/3}H_{2/3}O_4$' tetrahedra of the cubic compound are interconnected so as to form a three-dimensional structure, Fig. 1, in which each SO_4 is linked to three '$Li_{1/3}H_{2/3}O_4$' units and each '$Li_{1/3}H_{2/3}O_4$' is linked to four SO_4 tetrahedra.

The reanalysis of the structure of the compound formerly regarded as $Cs_{1.5}Li_{1.5}X(SO_4)_2$, where X = H or D, leads to a reexamination of the possible proton transport mechanism. Earlier, it was suggested that protons move along hydrogen bonded chains that extend along [111] via the reorientation of bisulfate groups and subsequent H transfer along asymmetric bonds, and that this reorientation was hindered by the presence of lithium ions. One would expect that even for the corrected structure, the overall steps of (HSO_4) group reorientation and proton transfer along hydrogen bonds apply, as they do to the majority of acid sulfate and selenate compounds [9]. In $Cs_3Li(XSO_4)_4$, bisulfate group reorientations are likely to occur around the [111] axes, moving protons from occupied to unoccupied hydrogen bonds. The close proximity of lithium ions to the normally unoccupied hydrogen bonds, 1.394(1) Å, would render this reorientation energetically unfavorable, and could explain the high activation energy for proton conductivity, ~ 1 eV [2].

5. Conclusions

The compound formerly reported to be $Cs_{1.5}Li_{1.5}X(SO_4)_2$ (X = H or D) has been shown here to have a true stoichiometry of $Cs_3Li(XSO_4)_4$. Sulfate groups in this compound are linked together either by pairs of hydrogen bonds or by a single LiO_4 tetrahedron. The hydrogen bonds nominally exist at two of the edges of the LiO_4 group, however, when the proton sites are occupied (and the hydrogen bonds present) the Li site is unoccupied and vice versa. The average Li site occupancy is $\frac{1}{3}$, the average hydrogen bond occupancy is $\frac{2}{3}$, and because of the double minimum in the hydrogen bond, the average D (or H) site occupancy is $\frac{1}{3}$. Despite the partial occupancies, $Cs_3Li(XSO_4)_4$ has a fixed overall stoichiometry. Proton transport is likely to occur via the reorientation of (HSO_4) groups about the [111] axes, bringing protons from occupied to otherwise unoccupied hydrogen bonds. As the latter sit, on average, on the edges of occupied LiO_4 tetrahedra, this reconfiguration must be associated with a large increase in energy, and may explain the high activation energy for proton conductivity. Thus, even the high cubic symmetry and the partial occupancy of the proton/deuterium ion sites are not sufficient to ensure 'superprotonic' conductivity in $Cs_3Li(XSO_4)_4$, as is known, for example, in the high temperature phase of $CsHSO_4$ [10].

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References

[1] B.V. Merinov, D.J. Jones, J. Roziere, Solid State Ionics 69 (1994) 53–58.
[2] B.V. Merinov, C.R.I Chisholm, D.A. Boysen, S.M. Haile, Solid State Ionics 145 (2001) 185–189.
[3] J. Baran, G. Bator, M. Drozd, M.M. Ilczyszyn, R. Jakubas, M.K. Marchewka, H. Ratajczak, J. Mol. Struct. 511–512 (1999) 1–18.
[4] J.-O. Lundgren, Crystallographic Computer Programs, Report UUIC-B13-4-05, Institute of Chemistry, University of Uppsala, Uppsala, Sweden, 1982.
[5] V.F. Sears, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, Vol. C, Kluwer, Dordrecht, 1993, pp. 383–391.
[6] M. Ichikawa, Acta Cryst. B 34 (1978) 2074–2080.
[7] I.D. Brown, Acta Cryst. A 32 (1976) 24–31.
[8] S.M. Haile, P.M. Calkins, J. Solid State Chem. 140 (1998) 251–265.
[9] S.M. Haile, K.D. Kreuer, J. Maier, Acta Cryst. B 51 (1995) 680–687.
[10] K.D. Kreuer, Solid State Ionics 94 (1997) 55–62.