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Synthesis, Structure, and Properties of Compounds in the $NaHSO_4$−$CsHSO_4$ System. 2. The Absence of Superprotonic Transitions in $Cs_2Na(HSO_4)_3$ 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, yielded the new compounds $CsNa_2(HSO_4)_3$ and $Cs_2Na(HSO_4)_3$. Thermal analysis demonstrated the absence of phase transitions for both compounds prior to melting. The conductivities of the two compounds vary monotonically with temperature, in a non-Arrhenius manner, from ambient to the respective melt temperatures of 398 and 413 K. At 363 K the conductivities are on the order of $10^{-8}\ \Omega^{1-}\mathrm{cm}^{-1}$, which is comparable to that of other alkali acid sulfates. The absence of transitions to disordered, high conductivity phases, as is observed in compounds such as $CsHSO_4$, is explained in terms of the stiffness of the Na−O bonds, which may serve to prevent rapid reorientation of SO_4 tetrahedral groups.

Introduction

Many solid acid sulfates and selenates undergo a variety of structural phase transitions in response to changes in temperature (or pressure). Many members of the $MHXO_4$ and $M_3H(XO_4)_2$ (M = alkali metal or ammonium ion, X = S or Se) families, in particular, exhibit transitions upon heating to highly disordered states that facilitate fast proton transport. The conductivity at the transition rises by 3−5 orders of magnitude, and, accordingly, both the transition and the electrical behavior are often termed "superprotonic". A widely recognized experimental observation is that only those solid acids containing large M cations (e.g., Cs, Rb, NH_4) exhibit superprotonic transitions. To date, no compelling explanation for the absence of such transitions for compounds of smaller alkali cations has been put forth, although Kreuer has proposed that large cations require large anion separations, which in turn lowers cation/anion and anion/anion interactions so as to promote tetrahedral group dynamics.[1] Alternatively, one might attribute the difference in behavior between, for example, $CsHSO_4$, which has a superprotonic transition at 414 K[2] and other $MHSO_4$ compounds, which simply melt upon heating (under atmospheric pressure) to their different crystal structures.[3−6] Recent results from the authors' laboratory demonstrating superprotonic transitions in $Cs_2(HSO_4)(H_2PO_4)$,[7] β-$Cs_3(HSO_4)_2[H_{2-x}(S_xP_{1-x})O_4]$,[8] and α-$Cs_3(HSO_4)_2(H_2PO_4)$,[9] each of which is structurally distinct, indicate, however, that superprotonic behavior is not unique to any particular structure type, and support the notion that the M^+ cation plays a significant role.

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 the nature of the cation and superprotonic phase transitions. The ultimate objective of these studies are to enable one to tune phase transitions and high-temperature behavior via judicious control of material chemistry. We report here, the second in a two-part series, the proton transport properties and thermal behavior of two new compounds discovered in this system, $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$. The crystal structures of these compounds have been presented in the first part of this series.[10]

Experimental Section and Results

Single crystals of $NaHSO_4$−$CsHSO_4$ compounds were obtained from aqueous solutions of cesium carbonate, sodium carbonate, and sulfuric acid. Solutions were prepared such that the molar ratio of the total alkali content to the SO_4 content was one to one, while the Cs:Na mole ratio was varied from 0:1 to 1:0 in increments of ~0.05. Solutions were maintained at room temperature and after 3−10 days of slow H_2O evaporation, large, transparent crystals were obtained. Phase identification of the resultant compounds was carried out by X-ray diffraction, using both powder and single-crystal methods. In addition to the known end-member compounds, $CsHSO_4$, $NaHSO_4$, and $NaHSO_4 \cdot H_2O$, two intermediate phases and one new structural form of $CsHSO_4$ were found. The compositions of the new mixed compounds, $Cs_2Na(HSO_4)_3$ (hexagonal)

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Table 1. Phases Obtained from Synthesis Experiments Carried out in the $CsHSO_4$–$NaHSO_4$ System

solution composition, % Na_2CO_3	compound(s) obtained
0	$CsHSO_4$ (phase-III)[3]
5–10	$CsHSO_4$ in new monoclinic form
15–35	$Cs_2Na(HSO_4)_3$
40	$Cs_2Na(HSO_4)_3$ + $CsNa_2(HSO_4)_3$
45–55	$CsNa_2(HSO_4)_3$
60–100	$NaHSO_4·H_2O$[12]

Table 2. Summary of Electron Probe Microanalysis Results of Cesium–Sodium Acid Sulfates

compound	anal. pts, no.	Cs, atom %[a]	Na, atom %[a]	S, atom %[a]	total wt %
$Cs_2Na(HSO_4)_3$	8	32.3 ± 3.5	16.9 ± 2.6	50.8 ± 3.2	72 ± 2.0
ideal	- -	33.3	16.7	50	66.4
$CsNa_2(HSO_4)_3$	11	16.0 ± 1.1	35.7 ± 1.1	48.3 ± 1.3	65.8 ± 1.5
ideal	- -	16.7	33.3	50	58.5

[a] As a percent of the total cation content, excluding protons.

and $CsNa_2(HSO_4)_3$ (cubic), were established by electron probe microanalysis, as described below, and confirmed by single-crystal structure determination, as reported in part one of this series. The structure of the new form of $CsHSO_4$, which grew from solutions with small sodium contents, is reported elsewhere. The crystalline phases obtained from each of the solutions is summarized in Table 1. In general, crystals of $Cs_2Na(HSO_4)_3$ grew as flattened rods of irregular cross-section, with dimensions as large as 3 × 10 × 20 mm^3 and the rod axis parallel to c. The crystals often contained liquid inclusions and were rather hydroscopic. Crystals of $CsNa_2(HSO_4)_3$ grew as large flat parallelepipeds with typical dimensions of 4 × 10 × 15 mm^3.

The composition of the new compounds was measured using a JEOL JXA-733 electron microprobe. Single crystals were mounted in an epoxy resin, polished, and then coated with carbon by evaporation. Microprobe data were collected at several positions on each sample for statistical averaging. Measured X-ray peak intensities were converted to elemental weight percentages using the CITZAF program.[11] High quality single crystals of the compounds CsH_2PO_4 and $Na_3H(SO_4)_2$ served as standards (grown in-house). The results of the analyses are presented in Table 2, and it is evident that the measured (normalized) values compare favorably to the ideal values. Moreover, the experimental error in any particular measurement was greater than the variation between results obtained at different positions on the sample, indicating that, within the measurement limits, the compounds were chemically homogeneous. The averaged, total, elemental cation weight % was somewhat greater than the expected value for each compound, Table 2. In light of the X-ray structural analysis, this observation was taken to be an artifact of the visible beam damage that occurred during data collection, rather than an error in the (relative) composition determination.

The high-temperature behavior of $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$ was examined using a Perkin-Elmer DSC 7 differential scanning calorimeter. For these measurements, samples were heated from 303 to 473 K under flowing nitrogen at heating rates which varied from 2 to 10 K/min. Representative results are presented in Figure 1. For both compounds there is only one transition, and in both cases, this is the melting transition (as established by visual inspection). Melting occurs at 398 K for $CsNa_2(HSO_4)_3$ and at 413 K for $Cs_2Na(HSO_4)_3$. The latter compound recrystallized upon cooling (as evident from the exothermic event in the cooling data), whereas the former solidified into an amorphous mass.

The conductivities of the mixed sodium–cesium solid acids were measured by a.c. impedance spectroscopy, using an HP 4284A LCR (inductance–capacitance–resistance) meter. Single-crystal samples were cut and polished, and, in the case of the hexagonal compound, $Cs_2Na(HSO_4)_3$, measurements were made both along and perpendicular to the *c*-axis. Silver paint (Ted Pella cat. no. 16032) served as the electrode material. Measurements were made over the frequency range 1 Hz to 1 MHz with an applied voltage of 1 V under dry argon. To eliminate the influence of surface adsorbed water on the conductivity measurements, data were collected over several heating/cooling cycles until the results were reproducible. Such a procedure also minimized the possibility that the measurements were influenced by surface decomposition. Heating and cooling rates were typically 0.5 K min^{-1}. The impedance spectra from both the polycrystalline and single-crystal sample in most cases exhibited a single arc in the Nyquist representation. The effective d.c. resistivity was determined by fitting the data to an (RQ) circuit using the least squares refinement program EQUIVCRT.[13] In Figure 2 the conductivities so measured are presented in Arrhenius form and compared to that of (polycrystalline) $CsHSO_4$ in its phase II form (space group $P2_1/c$).[14] In agreement with the thermal analyses, there are no transitions evident for either $Cs_2Na(HSO_4)_3$ or $CsNa_2(HSO_4)_3$ prior to melting.

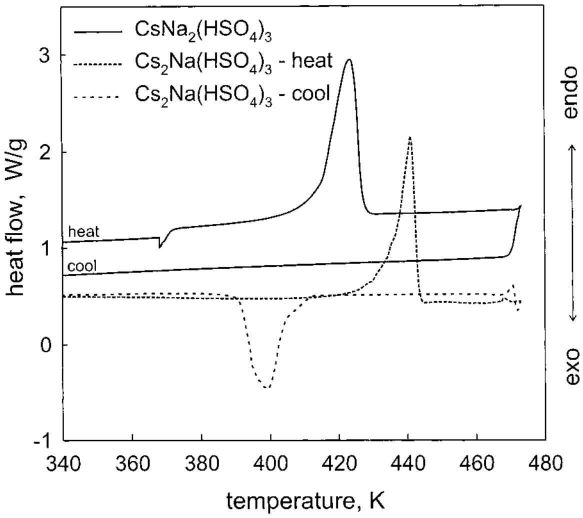

Figure 1. Differential scanning calorimetry traces of $Cs_2Na(HSO_4)_3$ (solid line) and $CsNa_2(HSO_4)_3$ (dashed line) obtained from heating/cooling cycles. Data collected under flowing N_2 at 10 K/min. For both materials, the endothermic peak obtained upon heating corresponds to the melt transition. The onset melting occurs at 413 K for $Cs_2Na(HSO_4)_3$ and at 398 K for $CsNa_2(HSO_4)_3$.

Discussion

In general, the magnitude of the conductivities of both $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$ are comparable to those of other nonsuperprotonic acid salts, such as $CsHSO_4$ below 414 K (Table 3). The magnitude of the temperature dependence is also within the typical range encountered. The anisotropy in the conductivity of $Cs_2Na(HSO_4)_3$, the hexagonal compound, is notable, as is the deviation from Arrhenius behavior for both compounds. Strongly non-Arrhenius behavior has been noted for $CsHSO_4$ at temperatures just below the superprotonic transition; the conductivity data in that case are well described by a critical temperature dependence with $\sigma \sim (T_o - T)^{-\gamma}$.[2] For the mixed cesium–

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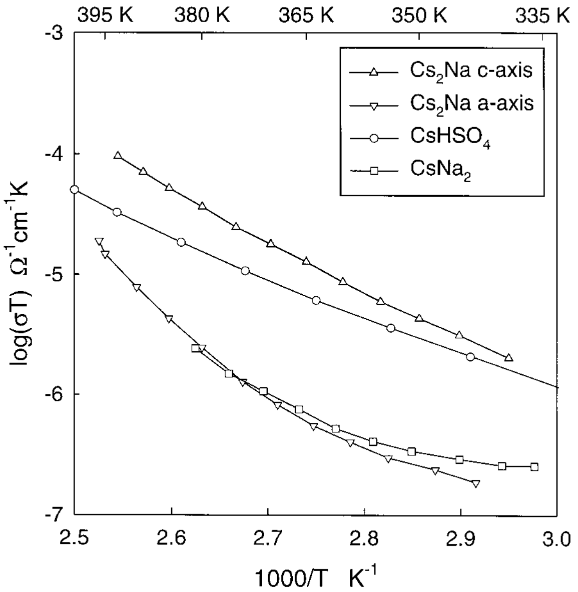

Figure 2. The conductivities of $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$ presented in Arrhenius form and compared to that of $CsHSO_4$. Both mixed cesium−sodium compounds were examined in single crystal form under dry argon. Data for $CsHSO_4$ are taken from Boysen et al.,[14] as measured from a polycrystalline sample. The superprotonic transition of $CsHSO_4$ occurs at 414 K, outside of the temperature region displayed.

Table 3. Electrical Properties of $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$[a]

compound	direction	E_σ, [eV]	log(A) $[\Omega^{-1}\,cm^{-1}\,K]$	σ (363 K) $[\Omega^{-1}\,cm^{-1}]$
$Cs_2Na(HSO_4)_3$	c-axis	0.82	6.39	3.1×10^{-8}
$Cs_2Na(HSO_4)_3$	a-axis	1.03	8.11	1.5×10^{-9}
$CsNa_2(HSO_4)_3$	(all)	0.2−1.2	−3.6−10.5	1.7×10^{-9}

[a] Activation energy and preexponential term taken from a linear regression fit of the data in Figure 2 to $\sigma = A/T \exp(-E_\sigma/k_bT)$ over the temperature range ~340−395 K. Arrhenius terms provided for comparison to literature data; measured conductivity exhibits highly non-Arrhenius behavior

sodium compounds, a power law does not provide an improved fit to the data over an Arrhenius law. It is likely that the observed curvature in the conductivity data, Figure 2, reflects the onset of the melting transition, which, in turn, may increase the concentration of mobile defects and the extent of their interaction with one another.

The significantly higher conductivity in $Cs_2Na(HSO_4)_3$ along its c-axis than that within the c-plane is a surprising result as the structure, at first glance, would seem to favor proton transport within the (0 0 1) plane. The crystal structure is formed of three-membered $(HSO_4)_3$ rings arranged in a two-dimensional hexagonal array. These arrays are stacked directly upon one another, with Cs and Na cations residing between them, to form the three-dimensional structure. In addition, there is disorder of the SO_4 tetrahedral group in that the O(3) atom is distributed over two neighboring sites, the first of which, O(31), serves as an acceptor in the hydrogen bond to O(1) and the second of which, O(32), is not involved in hydrogen bond formation. Typically, proton transport in solid acids involves proton hops along a double-minimum hydrogen bond and (HXO_4) group reorientation, giving rise to charge transport along hydrogen-bonded $H{-}OXO_{3\infty}$ chains (or within $[H_{1/2}XO_4]$ planes, in the case of $M_3H(XO_4)_2$ compounds). In $Cs_2Na(HSO_4)_3$, net charge transport requires, in addition to these steps, proton motion from one three-membered ring to the next. Such motion may be achieved by transient occupation of "interstitial" hydrogen bonds or proton sites. The shortest O···O distance between $(HSO_4)_3$ rings within the (0 0 1) plane is 2.97 Å [O(1) to O(2)], a distance that might be expected to correspond to such an interstitial site for charge transport perpendicular to the c-axis. The shortest comparable distance between $(HSO_4)_3$ rings in neighboring planes, controlling transport along c, is notably longer, 3.08 Å [O(32) to O(32)], with a second shortest distance of 3.09 Å [O(31) to O(32)]. The greater conductivity along c, despite the longer and presumably less favorable interstitial hydrogen-bond sites, suggests that the disorder about the O(3) atom plays a significant and beneficial role in proton transport.

The cubic compound, $CsNa_2(HSO_4)_3$, is also comprised of $(HSO_4)_3$ rings, in this case arranged in a pseudo-cubic close packed array. Cesium and sodium ions reside in the pseudo-octahedral and pseudo-tetrahedral interstitial sites, respectively, present within this array. The shortest O···O distance between sulfate trimer rings, that between O(1) and O(4), is 3.11 Å. The magnitude of the conductivity of the cubic compound is comparable to that of the hexagonal compound along its c-axis. The similarities between these two results suggests that the transport mechanisms in $CsNa_2(HSO_4)_3$ and along the c-axis of $Cs_2Na(HSO_4)_3$ are similar. This is consistent with the absence of structural disorder and of favorable proton interstitial sites in the cubic compound.

The absence of structural phase transitions in $CsNa_2(HSO_4)_3$ and especially $Cs_2Na(HSO_4)_3$ is a striking feature of their high-temperature behaviors. At the outset it was anticipated that the chemical similarity between $CsHSO_4$ and $Cs_2Na(HSO_4)_3$ would result in similar superprotonic properties and this unexpected result warrants some discussion. Despite the variety of structure-types across the $MHSO_4$ series, several structure-independent crystal-chemical measures can be examined to asses the role of the alkali ion in establishing material properties. These include the mean S···S, M···S, and M···M distances and the effective length per formula unit (taken as the cube root of the volume per formula unit). In Figure 3 these distances are plotted as a function of alkali ion size. In the case of the mixed cesium−sodium acid sulfates, the weighted average of the two alkali ionic radii have been used. While $Cs_2Na(HSO_4)_3$ has average M···M and S···S distances which are longer than those of $CsHSO_4$, the end-member sulfate has an M···S distance (4.17 Å) that is significantly greater than that of any of the other compounds, and even greater than the Cs···S distances in the cesium−sodium compounds. Of these various crystallographic distances, large S···S distances might be considered necessary in order to lower anion−anion interactions[1] and thereby promote the kind of rapid SO_4 reorientations that take place in superprotonic phases. The results here show that, in fact, either anion−anion interactions are not critical, or S···S distances are not a useful measure of such interactions.

The correlation evident in Figure 3 between M···S distance and superprotonic behavior may reflect a truly critical crystal−chemical parameter, or more likely

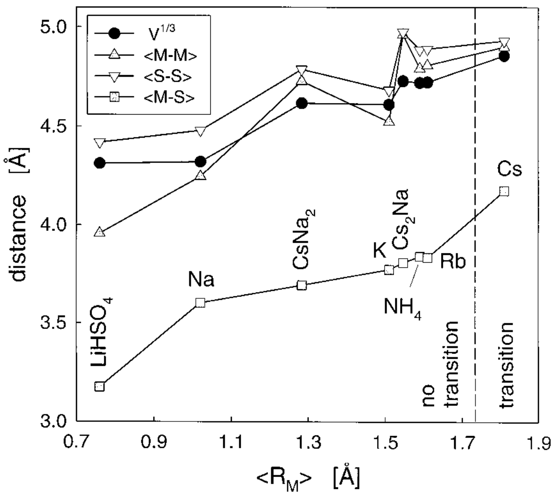

Figure 3. Characteristic lengths in alkali acid sulfates ($MHXO_4$ compounds) as a function of alkali ion radius. Crystallographic data taken from the following sources: $LiHSO_4$, Kemnitz et al.;[16] α-$NaHSO_4$, Sonneveld and Visser;[17] $KHSO_4$, Payan, and Haser;[6] $RbHSO_4$, Itoh et al.;[18] NH_4HSO_4, Nelmes;[5] $CsHSO_4$-II, Chisholm and Haile.[19] In the cesium−sodium compounds of the present work, the individual M−S distances depend strongly on the nature of the M species. The mean Cs−S and Na−S distances in $Cs_2Na(HSO_4)_3$ are 3.94 and 3.55 Å, respectively, whereas in $CsNa_2(HSO_4)_3$ they are 3.80 and 3.64 Å.

reflect the correlation of M···S distances with the nature of the M cation. Specifically, because the M−O−S angle is typically close to 120° (varying erratically with cation species from 100 to 145°), the M···S distance depends primarily on the M cation radius, which, in turn, correlates with such properties as alkali ion polarizability, strength of the M−O bond, and stiffness of the M−O bond.[15] Of these possible crystal−chemical parameters, we propose that it is the stiffness of the M−O bond which is critical in determining whether a compound can exist in a superprotonic phase in which the SO_4 groups undergo rapid reorientation. Soft M−O bonds, as occur in $CsHSO_4$, are more likely to accommodate the continuous reconfiguration of the MO_x coordination polyhedron that must accompany SO_4 group reorientation, than the stiff Na−O bonds which occur in $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$ in conjunction with Cs−O bonds.

Conclusions

Aqueous solutions of sodium carbonate, cesium carbonate, and sulfuric acid yield compounds of fixed composition. Partial substitution of cesium for sodium or vice versa is not observed within the experimental detection limits. Two new compounds intermediate compounds, $Cs_2Na(HSO_4)_3$ and $CsNa_2(HSO_4)_3$, have been obtained. Neither exhibits a superprotonic transition prior to melting at 398 and 413 K, respectively. The absence of such a transition is attributed to the stiffness of the Na−O bonds, which may hinder SO_4 reorientation, as would be necessary for superprotonic conductivity. The mean S···S distance in $Cs_2Na(HSO_4)_3$ is longer than that of $CsHSO_4$, a known superprotonic conductor, and thus widely separated sulfate groups cannot be sufficient for structural transitions to the disordered state and indeed may not be necessary at all. The absence of a crystallization transition for $CsNa_2(HSO_4)_3$ upon cooling from the melt suggests a route to amorphous acid sulfates with potentially novel properties.

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