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Sulfate Hydrides

Na₃SO₄H—The First Representative of the Material Class of Sulfate Hydrides

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Dedicated to Professor H. P. Beck on the occasion of his 80th birthday

Abstract: The first representative of a novel class of mixed-anionic compounds, the sulfate hydride Na₃SO₄H, and the corresponding deuteride Na₃SO₄D were obtained from the solid-state reaction of NaH or NaD with dry Na₂SO₄. Precise reaction control is required, because too harsh conditions lead to the reduction of sulfate to sulfide. A combined X-ray and neutron diffraction study revealed that the compound crystallizes in the tetragonal space group *P4/nmm* with the lattice parameters *a* = 7.0034(2) Å and *c* = 4.8569(2) Å. The sole presence of hydride and absence of hydroxide ions is proven by vibrational spectroscopy and comparison with spectra predicted from quantum chemical calculations. ¹H and ²³Na MAS NMR spectra are consistent with the structure of Na₃SO₄H: a single ¹H peak at 2.9 ppm is observed, while two peaks at 15.0 and 6.2 ppm for the inequivalent ²³Na sites are observed. Elemental analysis and quantum chemical calculations further support these results.

Whereas controlling the cation chemistry has been a tool to tune materials for many years, tailoring of the anion chemistry has recently become more and more important.^[1–5] Materials with desired physical and chemical properties can be obtained by taking advantage of the different anion radii, electronegativities or polarizabilities. Mainly during the last decade, this concept has become important due to the discovery of new mixed anionic hydrides. For instance, fast conductivity in a pure hydride anion conductor, La_{2–x–y}Sr_{x+y}LiH_{1–x+y}O_{3–y},^[6–10]

electronic conductivity in oxide hydride perovskite-type titanates,^[11–13] and even superconductivity^[14] were found in oxide hydrides. Tuning of the anion chemistry, for instance, allows for a tailoring of the bonding situations from more ionic to more covalent or varying the polarizabilities from rather hard to soft anions, tailoring crystal fields, or electronic properties.^[1] Very recently the novel material classes of phosphate hydrides,^[15,16] silicate hydrides,^[17,18] and borate hydrides^[19] were also discovered. Some mixed anionic hydrides, such as silicate hydrides, borate hydrides, oxide hydrides, and halide hydrides, also allowed for tuning of bright rare earth ion luminescence.^[17–25] Encouraged by these recent breakthroughs in an emerging field, we aimed to broaden our search for yet-to-be-discovered anion combinations with possibly unique chemical and physical properties. A possible candidate seemed to be the combination of sulfate and hydride anions, which, however, appeared to represent a synthetic challenge, since too reductive reaction conditions may be expected to reduce the sulfate anion instead of yielding the mixed anionic compound. Besides their importance in biological systems,^[26–28] sulfate anions also play an important role in inorganic materials, for instance exhibiting interesting optical properties, e.g., the non-linear optical compound K₄Sb(SO₄)₃Cl,^[29] materials for lanthanide-activated luminescence LnFSO₄·H₂O (Ln = Tb, Nd)^[30] or as candidates for solid state ion conduction.^[31,32]

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Herein, we report on the first representative of a novel anion combination, sulfate and hydride, $\text{Na}_3\text{SO}_4\text{H}$, synthetically accessible via a solid-state reaction of NaH with Na_2SO_4 under controlled conditions. For detailed experimental details see SI. A first structural model was obtained from powder X-ray diffraction using the program Jana2006.^[33] Due to the weak X-ray scattering ability of hydrides, it is necessary to additionally apply neutron diffraction in order to obtain a reliable structural model with hydride positions and occupation numbers.

Here, the bound coherent scattering cross section of ^2H (5.6 barn) is significant and also differs significantly from that of ^{23}Na (1.66 barn), ^{16}O (4.232 barn), and ^{32}S (1.0186 barn).^[34] The Rietveld refinement of the structure of deuterium-enriched $\text{Na}_3\text{SO}_4\text{D}$ using neutron powder data and X-ray diffraction data are depicted in Figures S1 and S2 in the SI.

$\text{Na}_3\text{SO}_4\text{D}$ was found to crystallize in the $\text{Ag}_3\text{CrO}_4\text{Cl}$ structure type^[35] in the tetragonal space group $P4/nmm$ (129)⁺ with the cell parameters $a = 7.0034(2)$ Å and $c = 4.8569(2)$ Å and is isotypic to the tungstate and molybdate chlorides $\text{Na}_3\text{MO}_4\text{Cl}$ ($\text{M} = \text{Mo}, \text{W}$,^[36] for detailed structural data see SI). Surprisingly, the structure does not show any similarity to the known fluoride analogues, as could be expected from the fluoride hydride analogy.^[37,38] In case of the fluorides, two phases of $\text{Na}_3\text{SO}_4\text{F}$ are known, a monoclinic ($P2_1/m$) low-temperature phase (α) and a trigonal ($R\bar{3}m$) high-temperature phase (β).^[32,39,40]

In the $\text{Na}_3\text{SO}_4\text{D}$ structure, two distinct sodium sites Na1 (4e) and Na2 (2c) exist with both sodium atoms being octahedrally surrounded by four oxygen and two deuterium/hydrogen atoms (see Figure 1 and Figure S4) resulting in two distinct $\text{D}_2\text{O}_4\text{Na}$ units.

While the octahedra around the Na1 position are interconnected via edge sharing, the octahedra surrounding the Na2 position are interconnected along the a and b axes via sulfate ions and corner sharing along the c axis. The deuteride ions are located within the octahedral voids built up by the sodium atoms forming DNA_6 subunits. In summary, the structure may also be described as a checkerboard pattern formed by a two-dimensional plane built up by the Na1 atoms. The planar-square fields of the Na1 atoms are then occupied

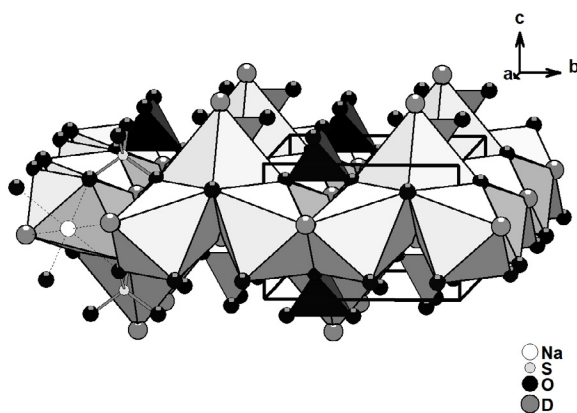


Figure 1. Crystal structure of $\text{Na}_3\text{SO}_4\text{D}$ along the a/b plane with coordination spheres of the cations.

chess-like either by sulfate tetrahedra or sodium Na2 (2c) and deuteride in an alternating order comparable to a checkerboard (Figures 1 and S3–S6).

Alternatively, the structure can also be described as an anti-perovskite-like structure. Here, the sulfate tetrahedra are located at the Ca sites and the hydride ions at the Ti sites, while the sodium atoms occupy the O sites (Figure 2). Anti-perovskite-like structures with tetrahedral building units are not uncommon, for example, $\text{K}_3\text{SO}_4\text{F}$ crystallizes in a similar anti-perovskite-like structure.^[41,42] Also minerals like the related anti-elpasolite-like sulfohalite $\text{Na}_6(\text{SO}_4)_2\text{ClF}$ are known to crystallize in such a manner.^[43]

In $\text{Na}_3\text{SO}_4\text{H}$, interatomic distances between deuteride/hydride and sodium ions are found to be between 2.25 and 2.61 Å, which is in the range of typical inorganic metal hydrides^[44] (e.g., NaH 2.4 Å^[45,46]). The S–O distance of 1.47 Å matches the typical interatomic S–O distance and covalent bond lengths of covalent sulfur–oxygen bonds of sulfate tetrahedra. The tetrahedral angles of 108.85–109.78° show only minor deviations compared to the ideal tetrahedron angle of 109.47°.^[47,48] The compound is susceptible to moisture. Contact with water shows visible formation of gas bubbles, which are tentatively assigned to the formation of H_2 or HD gas. However, it is possible to briefly expose the compound to dry air without decomposition or formation of hydrogen gas. Longer exposure to air and reaction with water result in a dissociation into Na_2SO_4 and $\text{Na}_4[\text{SO}_4]_{1.5}[\text{CO}_3]_{0.5}$, an indication that a likely hydroxide species $\text{Na}_3\text{SO}_4\text{OH}$ is not stable and indeed an air sensitive hydride is formed.

To support experimental findings, quantum chemical calculations using a hybrid density functional method have been performed. The crystal structure of $\text{Na}_3\text{SO}_4\text{H}$ was first optimized at the DFT-PBE0/TZVP level of theory (see Supporting Information for computational details). The optimized lattice parameters a and c differed from the experimental parameters by +0.1 % and –0.5 %, respectively. The optimized structure of $\text{Na}_3\text{SO}_4\text{H}$ was confirmed to be a true local minimum with no imaginary frequencies.

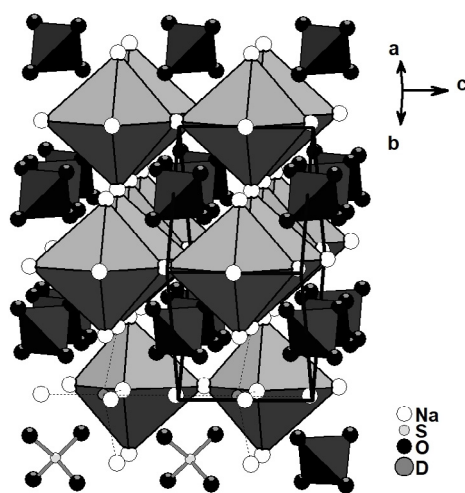


Figure 2. Alternative depiction of the crystal structure as an anti-perovskite-like structure. Here, the sulfate tetrahedra occupy the voids between the DNA_6 octahedra.

Electronic band structure and density of states (DOS) calculations suggest an insulating compound with an indirect band gap of 7.4 eV. The topmost valence bands are dominated by hydride anions, with minor contributions from the other atoms, which agrees with previous studies on mixed anionic hydrides.^[19] See Figure S13 for a detailed depiction of the electronic band structure and DOS. The reaction $\text{NaH} + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_3\text{SO}_4\text{H}$ is exoenergetic by 17 kJ mol⁻¹, showing that the formation of $\text{Na}_3\text{SO}_4\text{H}$ is energetically favorable (based on total energies at 0 K).

Because of its sensitivity to the local atomic-level structure, ¹H and ²³Na magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of $\text{Na}_3\text{SO}_4\text{H}$ were acquired to complement the average long-range structure determined from diffraction data discussed above. The ¹H MAS NMR spectrum (Figure 3a) is dominated by a single symmetric peak at $\delta_{\text{iso}} = 2.9$ ppm. The source of this peak is attributed to the hydride proton of the target compound, a similar value to the 4.3 ppm calculated at the DFT-PBE/USPP level of theory (see SI for computational details). The full width half maximum (fwhm) of 400 Hz for this peak is attributed primarily to incomplete decoupling of the heteronuclear ¹H-²³Na dipolar (through space) coupling from neighbouring ²³Na nuclei ($I = 3/2$, 100% natural abundance). A smaller peak (< 10% of the total intensity) at -4 ppm is thought to be due to hydride impurities from the starting materials, small amounts of amorphous hydridic or proton-containing side phases, such as, for example, hydrogen sulfate anions not

visible in the diffraction patterns; however, shielded ¹H nuclei for hydrides are also not uncommon.^[49] Figure 3b illustrates the experimental ²³Na MAS NMR spectrum for $\text{Na}_3\text{SO}_4\text{H}$ and the corresponding spectral simulation.

The sharp peak at 15.0 ppm is attributed to Na2, since the more symmetric environment (4 mm) about this nucleus is expected to yield a negligible quadrupolar coupling interaction (C_Q), as observed from the simulation (dotted trace). The broad asymmetric peak at $\delta = 6.2$ ppm (note that the signal position is affected by the second-order quadrupolar shift in Figure 3b) is attributed to Na1, which has a less symmetric octahedral environment (2/m). Here C_Q is determined to be 1.5 MHz, which is close to the DFT-PBE value of 1.85 MHz. The difference in the experimentally determined ²³Na isotropic chemical shifts between Na1 and Na2 (ppm) is found to be 8.8 ppm which is accurately predicted from theoretical ²³Na NMR calculation results, 9.9 ppm (Na1: $\delta_{\text{iso}} = -2.5$, Na2: $\delta_{\text{iso}} = 7.7$ ppm in reference to solid NaCl).

NMR spectra are consistent with the structure proposed via X-ray and neutron diffraction: a single hydrogen position is attributed to the hydride of $\text{Na}_3\text{SO}_4\text{H}$, and two ²³Na NMR sites are observed, with line shapes reflecting the local chemical environments about these nuclei.

To further confirm the hydridic character of the compound, as well as exclude the possibility of a hydroxide species, Raman and FT-IR spectroscopy were carried on both the hydride and deuteride-enriched samples. The experimental spectra were compared to spectra obtained with quantum chemical methods. Figure S10 shows the FT-IR spectrum in the region between 4000 and 450 cm⁻¹ with an enlarged inset of the typical OH-stretching vibration energies (3800–2250 cm⁻¹). No signal can be observed for such OH vibrations, indicating that the compound is indeed a hydroxide-free hydride.

As recently applied in the case of a novel borate hydride/deuteride, vibrational spectroscopy may also be a suitable tool to prove the presence of a mixed anionic hydride by hydride or deuteride modes and by comparison with calculated spectra.^[19] Replacing the hydride with a deuteride will usually lead to a shift of the energies to lower wavenumbers by a factor of $\sqrt{2}$ caused by the higher deuterium mass.

An enlarged view of the FT-IR spectrum (Figure 4) in the range from 1200 to 400 cm⁻¹ does indeed show a hydride out-of-plane mode (H^-_{op}) visible at 831 cm⁻¹, which is in good agreement with the band at 837 cm⁻¹ in the theoretical spectrum. The plane is defined by the square plane set up by the Na1 sodium atoms in the 4e site as depicted in Figure S12. Apart from this, hydride in-plane modes are clearly visible at 653 cm⁻¹ and 570 cm⁻¹ (H^-_{ip}), which fit to the theoretical values of 640 cm⁻¹ and 579 cm⁻¹, respectively. The $\text{H}^-_{\text{ip}}*$ mode describes hydride vibration coupled with sulfate bending modes.

Furthermore, besides hydride vibrations, vibrational bands corresponding to the sulfate ions are clearly visible and perfectly match the calculated bands. A detailed assignment of these bands can be found in the SI.

For the deuteride modes, a shift of nearly $\sqrt{2}$ can be observed, leading to the out-of-plane mode D^-_{op} appearing at 581 cm⁻¹ and the in-plane mode D^-_{ip} of the deuteride at

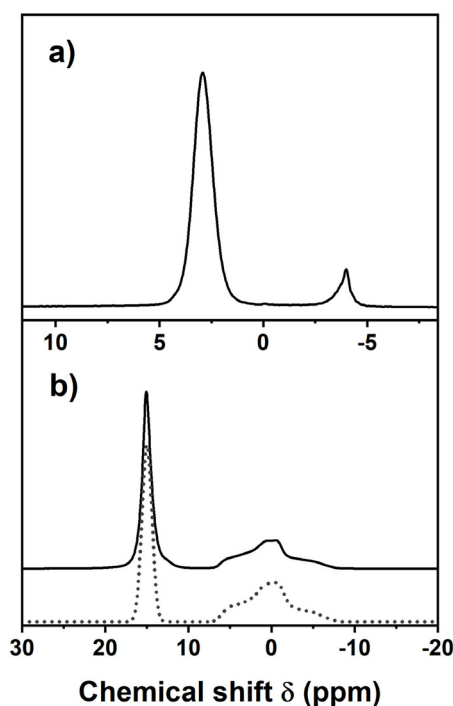


Figure 3. a) ¹H NMR spectrum of $\text{Na}_3\text{SO}_4\text{H}$, acquired at room temperature with a spinning frequency of 10.0 kHz, $B_0 = 9.4$ T, ¹H NMR chemical shifts at $\delta_{\text{H}} = 2.9$ ppm and $\delta = -3.9$ ppm. b) Simulation (dotted trace) and experimental (solid trace) ²³Na NMR spectra. Na1: $C_Q = 1.5$ MHz and $\eta = 0.74$, Na2: $C_Q = 0$ MHz, chemical shifts at $\delta_{\text{Na2}} = 15.0$ ppm and $\delta_{\text{Na1}} = 6.2$ ppm.

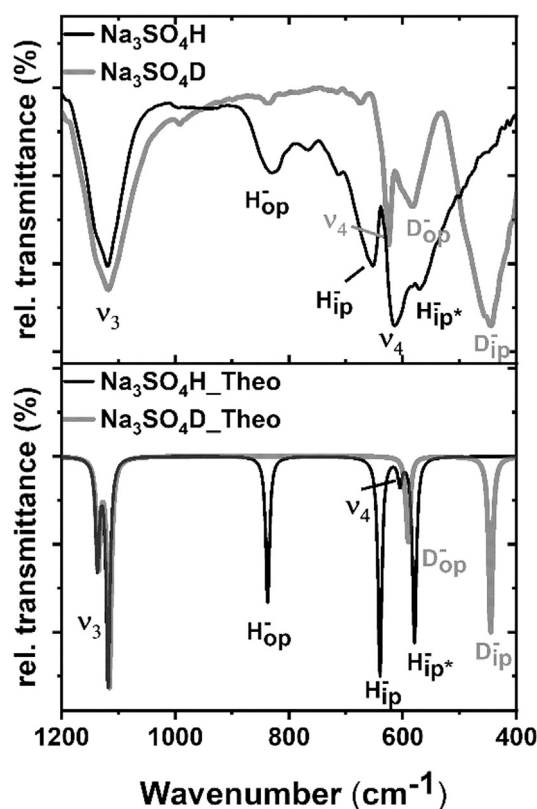


Figure 4. FT-IR spectra of $\text{Na}_3\text{SO}_4\text{H}$ and $\text{Na}_3\text{SO}_4\text{D}$ between 1200 cm^{-1} and 400 cm^{-1} (upper traces) in comparison to the theoretical FT-IR spectra of $\text{Na}_3\text{SO}_4\text{H}$ and $\text{Na}_3\text{SO}_4\text{D}$ (lower traces).

450 cm^{-1} . An additional signal at 600 cm^{-1} is tentatively assigned to the asymmetric bending mode of the sulfate that is predicted to be very weak in the theoretical spectrum. Raman spectra are depicted in Figure S11 and the assignment of the vibrational modes can be found in detail in the SI. The good agreement with calculated spectra reaffirms the presence of a novel sulfate hydride compound.

To further confirm the existence of hydrogen within the crystal lattice, elemental analysis has been conducted using a Vario El microanalyzer and the hot-gas extraction method. Here, the experimentally determined value of 0.61 wt% hydrogen matches almost perfectly to the theoretical value of 0.60 wt%.

In summary, the novel sulfate hydride $\text{Na}_3\text{SO}_4\text{H}$ was obtained by a simple solid-state reaction under controlled conditions. It crystallizes in the anti-perovskite-like $\text{Ag}_3\text{CrO}_4\text{Cl}$ structure type. The successful incorporation of hydride and the absence of hydroxide was proven by several independent methods, including X-ray and neutron powder diffraction, vibrational spectroscopy, solid-state NMR spectroscopy, elemental analysis, and quantum chemical calculations. To the best of our knowledge, such a combination of sulfate and hydride has not been realized so far, opening the door to a new class of mixed anionic hydrides, which may, in the future, be useful in different applications. For instance, especially if sulfate hydrides with di- or tri-valent cations can be found, such materials may be of interest for lanthanide-

activated optical materials. Furthermore, perovskite-like structures with the formulation of $\text{Na}_3\text{AO}_4\text{X}$ ($\text{A} = \text{S}, \text{Se}$; $\text{X} = \text{Cl}, \text{F}$) have been discussed as potential high-performance solid sodium ion electrolytes. Since it is known that in such solid-state electrolytes, the incorporation of polarizable anions may lead to better conduction properties,^[50,51] tuning of such materials using mixed-anionic hydrides may lead to promising materials for solid-state ion conduction in the future.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: anions · density functional calculations · hydrides · NMR spectroscopy

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