Borosulfates Hot Paper

Strong Lewis and Brønsted Acidic Sites in the Borosulfate Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$

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Abstract: *Borosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$ is the first borosulfate featuring a boron atom solely coordinated by three tetrahedra. Thus, the free Lewis acidic site forms a Lewis acid–base adduct with a water molecule. This is unprecedented for borosulfate chemistry and even for borates. Quantum chemical calculations on water exchange reactions with BF$_3$ and B(C$_6$F$_5$)$_3$ revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates. Additionally, Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$ was characterised by X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and density functional theory (DFT) calculations.*

Borosulfates are silicate-analogous materials featuring corner-sharing borate and sulfate tetrahedra.[1] Inspired by the rich crystal chemistry of silicates,[2] such substitution variants provide an extension of the structural variety and novel properties. Their sulfate tetrahedra lead to rather weak coordination behaviour[3] and might even give rise to high Brønsted acidity, as tetra(hydrogensulfato)boric acid H[B(HSO$_4$)$_4$] is known to be a superacid.[4] Furthermore, boron incorporation enables an even larger structural variety due to the possible presence of planar BO$_3$ moieties next to the BO$_4$ tetrahedra.[5] Moreover, such triangular coordinated boron atoms can serve as Lewis acidic centre as in the strong Lewis acids BF$_3$, BCl$_3$, B(C$_6$F$_5$)$_3$, or B(OSO$_2$CF$_3$)$_3$, which are

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important catalysts for various organic reactions such as Friedel–Crafts acylation or olefin polymerisation.[6,7]

However, in all hitherto reported borosulfates, the boron atom is coordinated tetrahedrally by four adjacent tetrahedra. The environment typically depends on the synthesis conditions: disulfate groups, that is, S–O–S bridges, occur using pure oleum (65% SO$_3$), alternating sulfate tetrahedra, that is, B–O–S bridges, occur in a mixture of oleum and sulfuric acid and corner-sharing borate tetrahedra, that is, B–O–B bridges, are obtained by synthesis mainly in sulfuric acid around 300°C.[8] Thus, we used low oleum concentration and moderate reaction temperatures at 180°C to obtain the unprecedented borosulfate Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$; this features a boron atom tri-coordinated by three sulfate groups—plus an additional water molecule. This may be understood as a Lewis acid–base adduct of water to a [B(SO$_4$)$_3$]$^{3-}$ moiety unknown so far to borate chemistry.

Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$ crystallises in a new structure type in space group $R\bar{3}$ (no. 148) with three formula units per unit cell at room temperature. Upon cooling the structure undergoes a symmetry descent towards the translationengleiche subgroup $P\bar{1}$ (no. 2) with one formula unit per unit cell (Figure 1a).[9] For convenience reasons, the following crystal structure description refers to the structure in $P\bar{1}$.[10] The structure can be described as a *hcp* packing of sulfate tetrahedra with half of the octahedral voids occupied by Mg^{2+} cations and a further third of these octahedral voids occupied by a boron–water adduct (Figure S10–S13). This results in the novel molecular anion [H$_2$O→B(SO$_4$)$_3$]$^{3-}$ which exhibits sorosilicate topology comparable to the open–branched triple tetrahedron {*oB*,3*t*}[Si$_4$O$_{13}$]$^{12-}$ anion in NaBa$_3$Nd$_3$[Si$_2$O$_7$][Si$_4$O$_{13}$].[2,11] A closer look suggests that [H$_2$O→B(SO$_4$)$_3$]$^{3-}$ is better described as a Lewis acid–base adduct of water to the [B(SO$_4$)$_3$]$^{3-}$ anion (Figure 1b). Thus, it is the very first example of a borosulfate in which a boron atom is only bound to three adjacent tetrahedra. The respective B–O^S bond lengths range from 143.6 to 144.4 pm—being somewhat shorter than in other borosulfates. The sulfate tetrahedra show elongated S–O bonds from 154.2 to 154.9 pm for the bridging ones and shorter bonds from 144.2 to 146.5 pm for the terminal ones. A slight elongation of the terminal S–O bonds can be observed for the oxygen atoms (O13, O23, O33) serving as acceptor in hydrogen bridging (Figure S14). The resulting free Lewis acidic site on the boron atom forms a water adduct. Hitherto, only non-condensed oxonium ions were observed in borosulfates.[12] Consequently, the B–O^H distance to the oxygen atom of the water molecule with 155.2 pm is significantly longer than the B–O^S bridging bonds towards the sulfate tetrahedra. The water molecule forms two moderate intermolecular

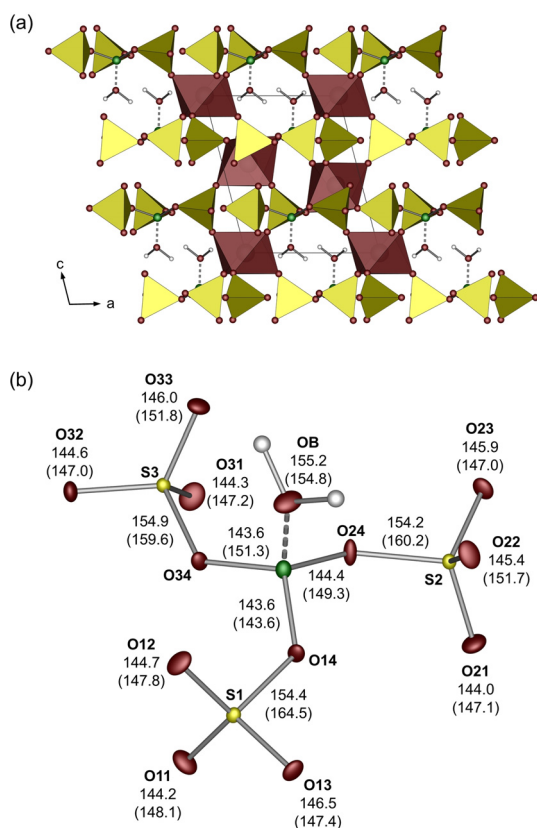*Figure 1.* a) Crystal structure of $Mg_3[H_2O \rightarrow B(SO_4)_3]_2$ viewed along *b* direction (sulfate tetrahedra, yellow; MgO_6 octahedra, red; boron atoms, green; hydrogen atoms, white) and b) $[H_2O \rightarrow B(SO_4)_3]^{3-}$ Lewis acid–base adduct with respective experimentally and (RI-)BP86/def2-TZVPP/D3(BJ) DFT-calculated (in parentheses) bond lengths in pm; ellipsoids are set to 70% probability.

hydrogen bonds and one rather weak intramolecular one; thus, all three sulfate tetrahedra are involved in hydrogen bonding (Figure S14, Table S9 and S10).[13] Looking into borophosphate chemistry, $Mg_2(H_2O)[BP_3O_9(OH)_4]$ contains a rather similar anion, viz. $[B(PO_4)(HPO_4)(H_2PO_4)(OH)]^{4-}$, featuring an OH^- group with a significantly shorter $B-O^H$ bond of 144.8 pm.[14] To the best of our knowledge, a water adduct is unprecedented in borophosphate and even in borate structural chemistry. The stabilisation of an adduct in borosulfates agrees with the strong electron withdrawing effect the attached sulfate groups exert on the Lewis acidic central boron atom. In addition, all attempts to shift one of the protons of the water adduct onto a sulfate unit, that is, as in $[HO-B(SO_3OH)(SO_4)_2]^{3-}$, led upon structure optimization at the D3(BJ) dispersion-corrected (RI-)BP86/def2-TZVPP DFT-level immediately to relaxation—and always gave the $[H_2O \rightarrow B(SO_4)_3]^{3-}$ adduct as the only and global minimum structure in this system (Figure 1 b). From DFT calculations with periodic boundary conditions (PBE-D3), a second local minimum with protonated $B-O-H$ and $S-O-H$ groups is obtained, but energetically disfavoured by 245 kJ mol^{-1} in comparison to the water adduct model.

Thus, these calculations confirmed the structure model of $Mg_3[H_2O \rightarrow B(SO_4)_3]_2$ (Table S38). Additionally, the calcu-

lated vibrational modes enable an assignment of bands in the infrared spectrum. The stretching modes $\nu(O-H)$ of the water molecule can be found at $\tilde{\nu} = 3357$ and 3215 cm^{-1}. These relatively low values indicate a weakening of the O–H bond and also a corresponding Brønsted acidity. The bending mode $\delta(H_2O)$ occurs at $\tilde{\nu} = 1614$ cm^{-1} and clearly proves the presence of the water molecule and excludes a possible combination of B(OH) and S(OH) groups, as it is in marked contrast to the S–O–H vibration modes present in $Cu[B(SO_4)_2(HSO_4)]$.[15] The bands between 1200 and 400 cm^{-1} can be assigned to stretching and bending vibrations of the anion (Figure S16 and S17, Table S13).

Regarding the Lewis acidic site, also the aforementioned strong Lewis acids boron trifluoride BF_3 and tris(pentafluorophenyl)-borane $B(C_6F_5)_3$ form water adducts. The $H_2O \rightarrow BF_3$ molecule[16] exhibits a rather ambiguous $B-O^H$ distance of 162.8 pm[17] whereas the $H_2O \rightarrow B(C_6F_5)_3$ molecule shows a $B-O^H$ distance of 160.8 pm.[18] To estimate the Lewis acidity of the $[B(SO_4)_3]^{3-}$ Lewis acid, isodesmic water exchange reactions of $[H_2O \rightarrow B(SO_4)_3]^{3-}$ with BF_3 and $B(C_6F_5)_3$ were calculated with the same method as before (Figure 2, (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level). In a reaction with BF_3, the water molecule is by $\Delta_r H = 29$ kJ mol^{-1} more strongly bound in the $[H_2O \rightarrow B(SO_4)_3]^{3-}$ anion and even by $\Delta_r H = 37$ kJ mol^{-1} upon reaction with $B(C_6F_5)_3$. The formal oxidation state $+VI$ of the sulfur atoms leads to a strong electron-withdrawing effect of the sulfate moieties in the $[B(SO_4)_3]^{3-}$ unit and consequently forms a stronger Lewis acid than the potent molecular counterparts BF_3 and $B(C_6F_5)_3$. This strongly attracts the σ-donating ligand H_2O and strengthens the $H_2O \rightarrow B$ interaction, which is also mirrored by the calculated $B-O^H$ distances: in $[H_2O \rightarrow B(SO_4)_3]^{3-}$ $d(B-O^H)$ is with 154.9 pm significantly shorter than that in $H_2O \rightarrow B(C_6F_5)_3$ (167.0 pm) and $H_2O \rightarrow BF_3$ (186.5 pm, Table S14).

The formation of a water adduct with a Lewis acid is generally accompanied by an increase of the Brønsted acidity. Thus, for an estimation of the Brønsted acidity, we also performed isodesmic and net isocharged calculations on proton exchange reactions of $[H_2O \rightarrow B(SO_4)_3]^{3-}$ with counter anions of similar size and same charge as the deprotonated form (Figure 3). In a reaction with the hypothetical $[Si_4O_{10}]^{4-}$ ion with P_4O_{10} topology, the proton is favoured by 67 kJ mol^{-1} on the side of the protonated silicate in $\Delta_r G°$. Consequently, the $[H_2O \rightarrow B(SO_4)_3]^{3-}$ anion is 11.7 orders of magnitude more acidic than the silicate anion. Note, an order of magnitude difference at standard conditions corresponds to a $\Delta_r G$ change of 5.71 kJ mol^{-1}.[19] Moreover, also in a reaction with the ultraphosphate anion $[P_4O_{12}]^{4-}$ the proton is more strongly bound to the phosphate by 37 kJ mol^{-1}, which corresponds to 6.5 orders of magnitude acidity. These findings agree with the formal oxidation state $+V$ for phosphorous and $+IV$ for silicon. Thus, $[H_2O \rightarrow B(SO_4)_3]^{3-}$ is indeed a considerably stronger acid, as expected due to the high Lewis acidity. This is also in line with the superacidic behaviour of the adduct $H_2O \rightarrow BF_3$[20] and the acidity of the adduct $H_2O \rightarrow B(C_6F_5)_3$, which can be compared to HCl.[18]

Moreover, for borosulfate chemistry, the tetra(hydrogensulfato)-boric acid $H[B(HSO_4)_4]$ was proven to be a super-

(a)

$\Delta H = 29$ kJ·mol^{-1}
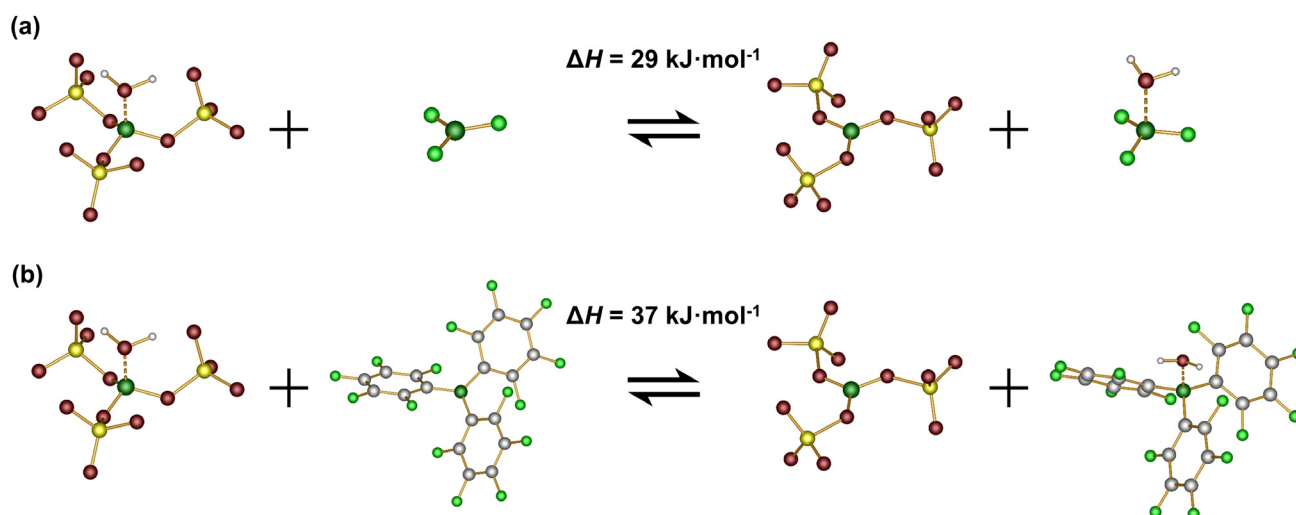
(b)

$\Delta H = 37$ kJ·mol^{-1}

Figure 2. Calculated isodesmic water exchange reactions of $[H_2O \rightarrow B(SO_4)_3]^{3-}$ with a) BF_3 and b) $B(C_6F_5)_3$ and the respective calculated enthalpy difference of the reaction calculated at the (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level.

(a)

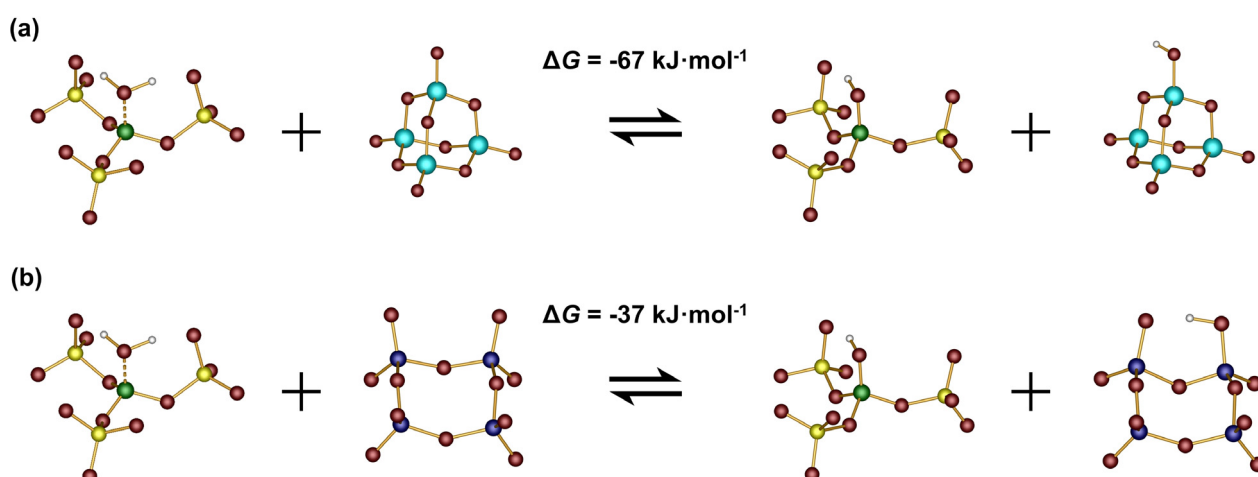$\Delta G = -67$ kJ·mol^{-1}

(b)

$\Delta G = -37$ kJ·mol^{-1}

Figure 3. Calculated isodesmic and isocharged proton exchange reactions of $[H_2O \rightarrow B(SO_4)_3]^{3-}$ with a) a hypothetical $[Si_4O_{10}]^{4-}$ anion and b) the $[P_4O_{12}]^{4-}$ anion and the respective calculated Gibbs free energy differences of the reactions calculated at the (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level.

acid[4,7] and calculations on $Cu[B(SO_4)_2(HSO_4)]$ also suggested a higher acidity than silicic acid.[15]

Finally, thermogravimetric analysis of $Mg_3[H_2O \rightarrow B(SO_4)_3]_2$ showed a stability up to 300°C before it transforms towards the known borosulfate β-$Mg_4[B_2O(SO_4)_6]$, which was additionally monitored by temperature-programmed X-ray diffraction. It is remarkable that this decomposition reaction can be understood as the condensation of two $[H_2O \rightarrow B(SO_4)_3]^{3-}$ Lewis acid–base adducts yielding a B−O−B bridge in a single $[B_2O(SO_4)_6]^{8-}$ anion.

In conclusion, we have presented the very first borosulfate containing a boron atom solely coordinated by three tetrahedra. The free Lewis site forms a Lewis acid–base adduct with water—unprecedented for borosulfate and even borate chemistry. Water and proton exchange reaction calculations revealed strong Lewis and Brønsted acidity. Thus, the title compound tremendously broadens the structural variety of borosulfates in general and yields fruitful insights into the exciting chemistry of borosulfates. Moreover, such a water adduct might give rise to the realisation of the first borosulfate with a planar BO_3 group or might be a highly interesting candidate for solid state catalysis and hence opens new horizons for borosulfate chemistry.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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[9] Crystal Data for HT-Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$: trigonal, $R\bar{3}$ (no. 148), $Z=3$, $a=796.200(10)$ pm, $c=2442.31(4)$ pm; crystal data for LT-Mg$_3$[H$_2$O→B(SO$_4$)$_3$]$_2$: triclinic, $P\bar{1}$ (no. 2), $Z=1$, $a=796.09(2)$ pm, $b=796.71(2)$ pm, $c=923.43(3)$ pm, $\alpha=64.9590(10)°$, $\beta=89.2280(10)°$, $\gamma=60.0540(10)°$; further details of the crystal structure investigations discussed in this contribu-

tion are listed in Tables S1–S9 in the Supporting Information and may be obtained from https://www.ccdc.cam.ac.uk/ on quoting the depository numbers 2051332 (HT) and 2048289 (LT), the names of the authors, and citation of this publication.

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