**Strong Lewis and Brønsted Acidic Sites in the Borosulfate**

Mg₃[H₂O→B(SO₄)₃]₂

Philip Netzsch, Regina Stroh, Florian Pielnhofer, Ingo Krossing, and Henning A. Höppe*

**Abstract:** Borosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates are silicate-alogous 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 interactions, and corner-sharing borate tetrahedra, that is, B-O-S bridges, occur in a mixture of oleum and sulfuric acid and corner-sharing borate tetrahedra, that is, Brønsted acidity than comparable silicates or phosphates.  

**Abstract:** Borosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.  

**B**orosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates. Mg₃[H₂O→B(SO₄)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 revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates.

---

[1] M. Sc. P. Netzsch, Prof. Dr. H. A. Höppe  
Lehrstuhl für Festkörperchemie  
Universität Augsburg  
Universitätsstrasse 1, 86159 Augsburg (Germany)  
E-mail: henning.hoeppe@physik.uni-augsburg.de

[2] M. Sc. R. Stroh, Prof. Dr. I. Krossing  
Institut für Anorganische und Analytische Chemie  
and Freiburger Materialforschungszentrum (FMF)  
Universität Freiburg  
Albertstrasse 21, 79104 Freiburg (Germany)

[3] Dr. F. Pielnhofer  
Institut für Anorganische Chemie  
Universität Regensburg  
Universitätsstrasse 31, 93053 Regensburg (Germany)

[4] Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:  
https://doi.org/10.1002/anie.202016920.

[5] © 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.
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, Mg₃[H₂O*B(SO₄)₃]₃ contains a rather similar anion, viz. \( \text{B(PO₄)₃(HPO₄)(H₂PO₄)(OH)} \), featuring an OH⁻ group with a significantly shorter B–O⁻ 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 borophosphate chemistry, Mg₂(H₂O)[BP₃O₉(OH)₄] contains a rather similar anion, viz. \( \text{[B(PO₄)(HPO₄)(H₂PO₄)(OH)} \)₄, 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 Mg₃[H₂O*B(SO₄)₃]₃ (Table S38). Additionally, the calculated vibrational modes enable an assignment of bands in the infrared spectrum. The stretching modes ν(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 δ(H₂O) occurs at \( \tilde{\delta} = 1614 \) 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(SO₄)₂(HSO₄)].[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 BF₃ and tris(pentafluorophenyl)-borane B(C₆F₅)₃ form water adducts. The H₂O→BF₃ molecule[16] exhibits a rather ambiguous B–O⁻ distance of 162.8 pm[17] whereas the H₂O→B(C₆F₅)₃ molecule shows a B–O⁻ distance of 160.8 pm.[18] To estimate the Lewis acidity of the [B(SO₄)₃]²⁻ Lewis acid, isodesmic water exchange reactions of \( [\text{H₂O→B(SO₄)₃}]^{+}\) with BF₃ and B(C₆F₅)₃ were calculated with the same method as before (Figure 2, (R1)-BP86/def2-TZVPP/D3(BJ) DFT-level). In a reaction with BF₃, the water molecule is by ΔH = 29 kJ mol⁻¹ more strongly bound in the [H₂O→B(SO₄)₃]²⁻ anion and even by ΔH = 37 kJ mol⁻¹ upon reaction with B(C₆F₅)₃. The formal oxidation state + VI of the sulfur atoms leads to a strong electron-withdrawing effect of the sulfate moieties in the [B(SO₄)₃]²⁻ unit and consequently forms a stronger Lewis acid than the potent molecular counterparts BF₃ and B(C₆F₅)₃. This strongly attracts the σ-donating ligand H₂O and strengthens the H₂O–B interaction, which is also mirrored by the calculated B–O⁻ distances: in \( [\text{H₂O→B(SO₄)}]^{+}\) d(B–O⁻) is with 154.9 pm significantly shorter than that in H₂O→B(C₆F₅)₃ (167.0 pm) and H₂O→BF₃ (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 \( [\text{H₂O→B(SO₄)}]^{+}\) with counter anions of similar size and same charge as the deprotonated form (Figure 3). In a reaction with the hypothetical [SiO₄]³⁻ anion with P₂O₅ topology, the proton is favoured by 67 kJ mol⁻¹ on the side of the protonated silicate in ΔG°. Consequently, the [H₂O→B(SO₄)]²⁻ 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 ΔG change of 5.71 kJ mol⁻¹[19]. Moreover, also in a reaction with the ultraphosphate anion [P₂O₇]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, \( [\text{H₂O→B(SO₄)}]^{+}\) 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 H₂O→BF₃[20] and the acidity of the adduct H₂O→B(C₆F₅)₃, which can be compared to HCl.[20] Moreover, for borosulfate chemistry, the tetra(hydrogensulfato)boric acid H[B(HSO₄)]₄ was proven to be a super-
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$_2$O ! B(SO$_4$)$_3$)$_2$ showed a stability up to 300 °C before it transforms towards the known borosulfate β-Mg$_4$[B$_2$O(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$_2$O ! B(SO$_4$)$_3$]$_3$ Lewis acid–base adducts yielding a B–O–B bridge in a single [B$_2$O(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**

The authors thank the Deutsche Forschungsgemeinschaft (DFG) for financial support under the project HO 4503/5-1. F.P. thanks Prof. Bettina Lotsch, Dr. Ulrich Wedig and the Computer Service group from the Max-Planck-Institute for Solid State Research (Stuttgart, Germany) for access to computational facilities Open access funding enabled and organized by Projekt DEAL.
Conflict of interest

The authors declare no conflict of interest.

Keywords: borosulfates · Brønsted acid · Lewis acid · Lewis acid base adduct · silicate analogue

[1] a) J. Bruns, H. A. Höppe, M. Daub, H. Hillebrecht, H. Huppertz, Chem. Eur. J. 2020, 26, 7966; b) H. A. Hoppe, K. Kazmierczak, M. Daub, K. Forg, F. Fuchs, H. Hillebrecht, Angew. Chem. Int. Ed. 2012, 51, 6255; Angew. Chem. 2012, 124, 6359.
[2] F. Liebau, Structural Chemistry of Silicates, Springer, Heidelberg, 1985.
[3] a) P. Netzsch, P. Gross, H. Takahashi, H. A. Hoppe, Inorg. Chem. 2018, 57, 8530; b) P. Netzsch, M. Hämmer, P. Gross, H. Bariass, T. Block, L. Ulett, R. Pottgen, J. Bruns, H. Huppertz, H. A. Hoppe, Dalton Trans. 2019, 48, 4387; c) P. Netzsch, F. Pielnhofer, R. Glaum, H. A. Hoppe, Chem. Eur. J. 2020, 26, 14745.
[4] R. J. Gillespie, T. E. Pedl, E. A. Robinson, J. Am. Chem. Soc. 1971, 93, 5083.
[5] M. Mutailipu, K. R. Poeppelmeier, S. Pan, Chem. Rev. 2021, 121, 1130.
[6] a) W. E. Piers, T. Chivers, Chem. Soc. Rev. 1997, 26, 345; b) W. E. Piers, Adv. Organomet. Chem. 2004, 52, 1; c) G. A. Olah, O. Farooq, S. M. F. Farnia, J. A. Olah, J. Am. Chem. Soc. 1988, 110, 2560; d) A. Corma, H. Garcia, Chem. Rev. 2003, 103, 4307; e) I. B. Sivaev, V. I. Bregadze, Coord. Chem. Rev. 2014, 270–271, 75.
[7] G. A. Olah, G. K. S. Prakash, Å. Molnár, J. Sommer, Superacid chemistry, Wiley, Hoboken, 2009.
[8] a) P. Netzsch, F. Pielnhofer, H. A. Hoppe, Inorg. Chem. 2020, 59, 15180; b) P. Netzsch, H. A. Hoppe, Inorg. Chem. 2020, 59, 18102.

Crystal Data for HT-Mg₃H₂O·2B(SO₄)₃·H₂O (R₁), the names of the authors, and citation of this publication.

Manuscript received: December 21, 2020
Accepted manuscript online: March 10, 2021
Version of record online: March 30, 2021