


**Borosulfates Hot Paper**
How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 10643–10646

International Edition: doi.org/10.1002/anie.202016920

German Edition: doi.org/10.1002/ange.202016920

# Strong Lewis and Brønsted Acidic Sites in the Borosulfate $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$

Philip Netzsch, Regina Stroh, Florian Pielhofer, Ingo Krossing, and Henning A. Höpfe\*

**Abstract:** Borosulfates provide fascinating structures and properties that go beyond a pure analogy to silicates.  $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$  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  $\text{BF}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  revealed a higher Lewis acidity for the borosulfate anion. Moreover, proton exchange reactions showed a higher Brønsted acidity than comparable silicates or phosphates. Additionally,  $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$  was characterised by X-ray diffraction, infrared spectroscopy, thermogravimetric analysis, and density functional theory (DFT) calculations.

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

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

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%  $\text{SO}_3$ ), 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.<sup>[8]</sup> Thus, we used low oleum concentration and moderate reaction temperatures at 180 °C to obtain the unprecedented borosulfate  $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$ ; 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  $[\text{B}(\text{SO}_4)_3]^{3-}$  moiety unknown so far to borate chemistry.

$\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$  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 1 a).<sup>[9]</sup> For convenience reasons, the following crystal structure description refers to the structure in  $P\bar{1}$ .<sup>[10]</sup> The structure can be described as a *hcp* packing of sulfate tetrahedra with half of the octahedral voids occupied by  $\text{Mg}^{2+}$  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  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  which exhibits sorosilicate topology comparable to the open-branched triple tetrahedron  $\{\text{oB}, 3\text{t}\}[\text{Si}_4\text{O}_{13}]^{12-}$  anion in  $\text{NaBa}_3\text{Nd}_3[\text{Si}_2\text{O}_7][\text{Si}_4\text{O}_{13}]$ .<sup>[2,11]</sup> A closer look suggests that  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  is better described as a Lewis acid–base adduct of water to the  $[\text{B}(\text{SO}_4)_3]^{3-}$  anion (Figure 1 b). 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<sup>s</sup> 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.<sup>[12]</sup> Consequently, the B–O<sup>H</sup> distance to the oxygen atom of the water molecule with 155.2 pm is significantly longer than the B–O<sup>s</sup> bridging bonds towards the sulfate tetrahedra. The water molecule forms two moderate intermolecular

[\*] M. Sc. P. Netzsch, Prof. Dr. H. A. Höpfe

Lehrstuhl für Festkörperchemie

Universität Augsburg

Universitätsstrasse 1, 86159 Augsburg (Germany)

E-mail: henning.hoeppe@physik.uni-augsburg.de

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)

Dr. F. Pielhofer

Institut für Anorganische Chemie

Universität Regensburg

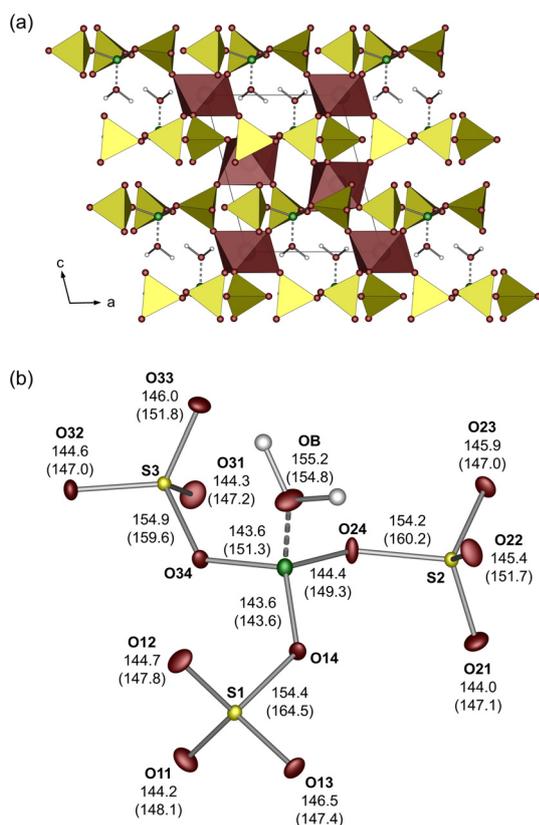
Universitätsstrasse 31, 93053 Regensburg (Germany)

 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>


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**Figure 1.** a) Crystal structure of  $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$  viewed along  $b$  direction (sulfate tetrahedra, yellow;  $\text{MgO}_6$  octahedra, red; boron atoms, green; hydrogen atoms, white) and b)  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  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).<sup>[13]</sup> Looking into borophosphate chemistry,  $\text{Mg}_2(\text{H}_2\text{O})[\text{BP}_3\text{O}_9(\text{OH})_4]$  contains a rather similar anion, viz.  $[\text{B}(\text{PO}_4)(\text{HPO}_4)(\text{H}_2\text{PO}_4)(\text{OH})]^{4-}$ , featuring an  $\text{OH}^-$  group with a significantly shorter  $\text{B}-\text{O}^{\text{H}}$  bond of 144.8 pm.<sup>[14]</sup> 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  $[\text{HO}-\text{B}(\text{SO}_3\text{OH})(\text{SO}_4)_2]^{3-}$ , led upon structure optimization at the D3(BJ) dispersion-corrected (RI-)BP86/def2-TZVPP DFT-level immediately to relaxation—and always gave the  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  adduct as the only and global minimum structure in this system (Figure 1b). From DFT calculations with periodic boundary conditions (PBE-D3), a second local minimum with protonated  $\text{B}-\text{O}-\text{H}$  and  $\text{S}-\text{O}-\text{H}$  groups is obtained, but energetically disfavoured by 245  $\text{kJ mol}^{-1}$  in comparison to the water adduct model.

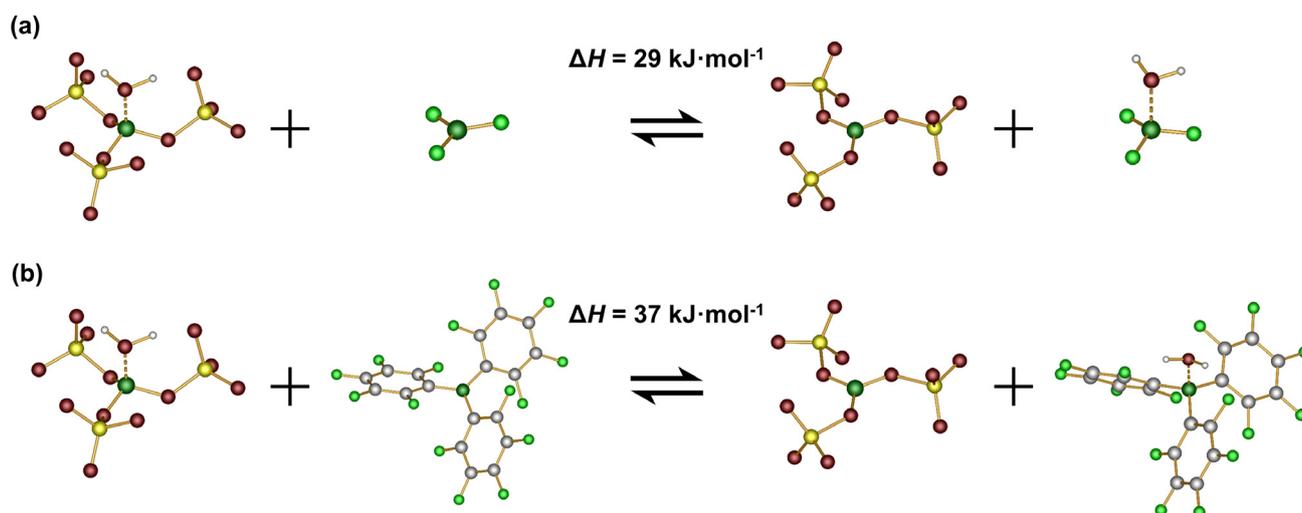
Thus, these calculations confirmed the structure model of  $\text{Mg}_3[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]_2$  (Table S38). Additionally, the calcu-

lated vibrational modes enable an assignment of bands in the infrared spectrum. The stretching modes  $\nu(\text{O}-\text{H})$  of the water molecule can be found at  $\tilde{\nu} = 3357$  and  $3215 \text{ cm}^{-1}$ . These relatively low values indicate a weakening of the  $\text{O}-\text{H}$  bond and also a corresponding Brønsted acidity. The bending mode  $\delta(\text{H}_2\text{O})$  occurs at  $\tilde{\nu} = 1614 \text{ cm}^{-1}$  and clearly proves the presence of the water molecule and excludes a possible combination of  $\text{B}(\text{OH})$  and  $\text{S}(\text{OH})$  groups, as it is in marked contrast to the  $\text{S}-\text{O}-\text{H}$  vibration modes present in  $\text{Cu}[\text{B}(\text{SO}_4)_2(\text{HSO}_4)]$ .<sup>[15]</sup> The bands between 1200 and  $400 \text{ cm}^{-1}$  can be assigned to stretching and bending vibrations of the anion (Figure S16 and S17, Table S13).

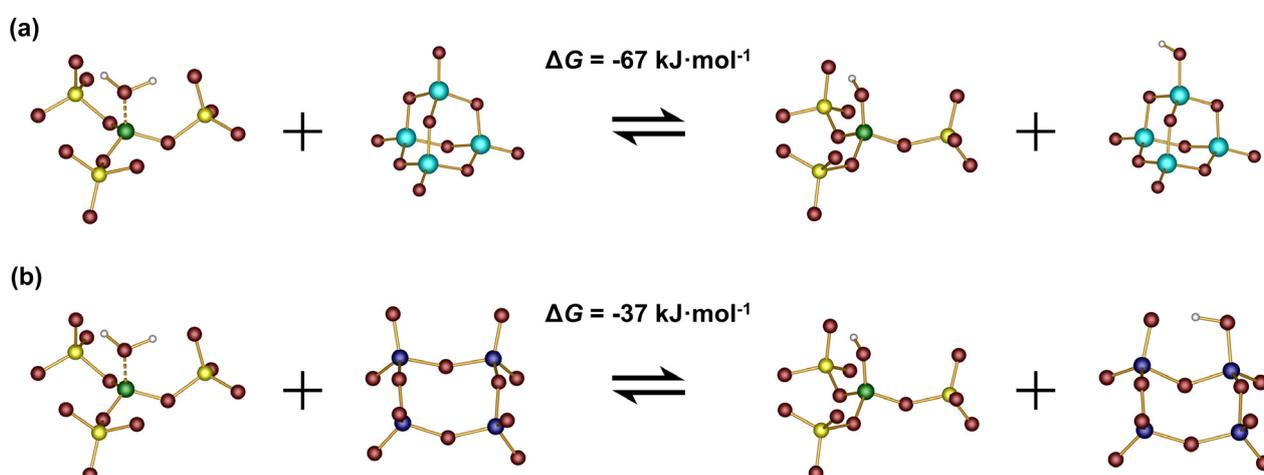
Regarding the Lewis acidic site, also the aforementioned strong Lewis acids boron trifluoride  $\text{BF}_3$  and tris(pentafluorophenyl)-borane  $\text{B}(\text{C}_6\text{F}_5)_3$  form water adducts. The  $\text{H}_2\text{O} \rightarrow \text{BF}_3$  molecule<sup>[16]</sup> exhibits a rather ambiguous  $\text{B}-\text{O}^{\text{H}}$  distance of 162.8 pm<sup>[17]</sup> whereas the  $\text{H}_2\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$  molecule shows a  $\text{B}-\text{O}^{\text{H}}$  distance of 160.8 pm.<sup>[18]</sup> To estimate the Lewis acidity of the  $[\text{B}(\text{SO}_4)_3]^{3-}$  Lewis acid, isodesmic water exchange reactions of  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  with  $\text{BF}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  were calculated with the same method as before (Figure 2, (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level). In a reaction with  $\text{BF}_3$ , the water molecule is by  $\Delta_r H = 29 \text{ kJ mol}^{-1}$  more strongly bound in the  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  anion and even by  $\Delta_r H = 37 \text{ kJ mol}^{-1}$  upon reaction with  $\text{B}(\text{C}_6\text{F}_5)_3$ . The formal oxidation state +VI of the sulfur atoms leads to a strong electron-withdrawing effect of the sulfate moieties in the  $[\text{B}(\text{SO}_4)_3]^{3-}$  unit and consequently forms a stronger Lewis acid than the potent molecular counterparts  $\text{BF}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ . This strongly attracts the  $\sigma$ -donating ligand  $\text{H}_2\text{O}$  and strengthens the  $\text{H}_2\text{O} \rightarrow \text{B}$  interaction, which is also mirrored by the calculated  $\text{B}-\text{O}^{\text{H}}$  distances: in  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$   $d(\text{B}-\text{O}^{\text{H}})$  is with 154.9 pm significantly shorter than that in  $\text{H}_2\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$  (167.0 pm) and  $\text{H}_2\text{O} \rightarrow \text{BF}_3$  (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  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  with counter anions of similar size and same charge as the deprotonated form (Figure 3). In a reaction with the hypothetical  $[\text{Si}_4\text{O}_{10}]^{4-}$  ion with  $\text{P}_4\text{O}_{10}$  topology, the proton is favoured by 67  $\text{kJ mol}^{-1}$  on the side of the protonated silicate in  $\Delta_r G^\circ$ . Consequently, the  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  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  $\text{kJ mol}^{-1}$ .<sup>[19]</sup> Moreover, also in a reaction with the ultraphosphate anion  $[\text{P}_4\text{O}_{12}]^{4-}$  the proton is more strongly bound to the phosphate by 37  $\text{kJ mol}^{-1}$ , 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,  $[\text{H}_2\text{O} \rightarrow \text{B}(\text{SO}_4)_3]^{3-}$  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  $\text{H}_2\text{O} \rightarrow \text{BF}_3$ <sup>[20]</sup> and the acidity of the adduct  $\text{H}_2\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$ , which can be compared to  $\text{HCl}$ .<sup>[18]</sup>

Moreover, for borosulfate chemistry, the tetra(hydrogen-sulfato)-boric acid  $\text{H}[\text{B}(\text{HSO}_4)_4]$  was proven to be a super-



**Figure 2.** Calculated isodesmic water exchange reactions of  $[\text{H}_2\text{O}\rightarrow\text{B}(\text{SO}_4)_3]^{3-}$  with a)  $\text{BF}_3$  and b)  $\text{B}(\text{C}_6\text{F}_5)_3$  and the respective calculated enthalpy difference of the reaction calculated at the (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level.



**Figure 3.** Calculated isodesmic and isocharged proton exchange reactions of  $[\text{H}_2\text{O}\rightarrow\text{B}(\text{SO}_4)_3]^{3-}$  with a) a hypothetical  $[\text{Si}_4\text{O}_{10}]^{4-}$  anion and b) the  $[\text{P}_4\text{O}_{12}]^{4-}$  anion and the respective calculated Gibbs free energy differences of the reactions calculated at the (RI-)BP86/def2-TZVPP/D3(BJ) DFT-level.

acid<sup>[4,7]</sup> and calculations on  $\text{Cu}[\text{B}(\text{SO}_4)_2(\text{HSO}_4)]$  also suggested a higher acidity than silicic acid.<sup>[15]</sup>

Finally, thermogravimetric analysis of  $\text{Mg}_3[\text{H}_2\text{O}\rightarrow\text{B}(\text{SO}_4)_3]_2$  showed a stability up to 300°C before it transforms towards the known borosulfate  $\beta\text{-Mg}_4[\text{B}_2\text{O}(\text{SO}_4)_6]$ , 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  $[\text{H}_2\text{O}\rightarrow\text{B}(\text{SO}_4)_3]^{3-}$  Lewis acid–base adducts yielding a B–O–B bridge in a single  $[\text{B}_2\text{O}(\text{SO}_4)_6]^{8-}$  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  $\text{BO}_3$  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

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- [9] Crystal Data for HT-Mg<sub>3</sub>[H<sub>2</sub>O→B(SO<sub>4</sub>)<sub>3</sub>]<sub>2</sub>: trigonal, *R* $\bar{3}$  (no. 148), *Z* = 3, *a* = 796.200(10) pm, *c* = 2442.31(4) pm; crystal data for LT-Mg<sub>3</sub>[H<sub>2</sub>O→B(SO<sub>4</sub>)<sub>3</sub>]<sub>2</sub>: 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 contribution 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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Manuscript received: December 21, 2020  
Accepted manuscript online: March 10, 2021  
Version of record online: March 30, 2021