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# Cd[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] and H<sub>2</sub>[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] – a phyllosilicate-analogous borosulfate and its homeotypic heteropolyacid†

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Borosulfates consist of heteropolyanionic networks of corner-shared (SO<sub>4</sub>)- and (BO<sub>4</sub>)-tetrahedra charge compensated by metal or non-metal cations. The anionic substructures differ significantly, depending on the different branching of the silicate-analogous borosulfate building blocks. However, only one acid has been characterized by single crystal X-ray diffraction so far. Herein, we present H<sub>2</sub>[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] as the first phyllosilicate analogue representative, together with the homeotypic representative Cd[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>]. The latter can be considered the cadmium salt of the former. Their crystal structures and crystallographic relationship are elucidated. For H<sub>2</sub>[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>], the bonding situation is examined using Hirshfeld-surface analysis. Further, the optical and thermal properties of Cd[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] are investigated by FTIR and UV-Vis spectroscopy, thermogravimetry, as well as temperature-programmed powder X-ray diffraction.

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## Introduction

In recent years, interest in borosulfates has been growing steadily, not only due to their structural versatility<sup>1</sup> but also for their potential applications in the fields of solid acid electrolytes and SHG materials.<sup>2–4</sup> The anionic substructures of borosulfates are similar to silicates and consist – except for rare cases<sup>4–6</sup> – of (SO<sub>4</sub>)- and (BO<sub>4</sub>)-tetrahedra connected *via* one common vertex. Accordingly, oligomeric anions like in K<sub>5</sub>[B(SO<sub>4</sub>)<sub>4</sub>],<sup>7</sup> which was the first reported representative, anionic chains<sup>8–15</sup> and layers<sup>16–18</sup> as well as extended 3D network structures<sup>2,8</sup> have been presented. In contrast to aluminosulfates, where Al–O–Al bonds are unexpected according to Loewenstein's rule<sup>19</sup> and in violation of Pauling's rules,<sup>20</sup> several so-called unconventional borosulfates with B–O–B<sup>15,21–24</sup> and even S–O–S<sup>8,11,25–27</sup> bridges are known. Hitherto, borosulfates with anionic chains are particularly numerous, whereas 3D networks are especially scarce. In contrast to the structural diversity of the anionic substructure, which is expected to be growing even bigger, the nature of the charge-

compensating cations is so far limited. Although, compounds with cations of different valence (monovalent up to trivalent) are known, apart from ammonium,<sup>9</sup> oxonium,<sup>2,11</sup> and two heteropolycationic Au–Cl species<sup>28</sup> the cations are only monatomic. Considering the special segment of the conventional borosulfates with phyllosilicate-analogous topology, *i.e.* with infinite two dimensional heteropolyanions, only structures with divalent cations have been reported so far. They generally follow the composition M[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] with M = Mg<sup>2+</sup>,<sup>15</sup> Ca<sup>2+</sup>,<sup>29</sup> Co<sup>2+</sup>,<sup>17,18</sup> Ni<sup>2+</sup>,<sup>17</sup> Zn<sup>2+</sup>,<sup>30</sup> Mn<sup>2+</sup>,<sup>30</sup> Cu<sup>2+</sup>.<sup>31</sup> All of these compounds share the structural motif of connected *zwölfer* and *vierer* rings, consisting of alternating (BO<sub>4</sub>)- and (SO<sub>4</sub>)-tetrahedra as their heteropolyanion. This set of compounds can be grouped by the adapted crystal structure differing in the location of the cations in the structure. They are located either within the *zwölfer* ring of the anionic layer (Mg<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>) or between adjacent layers (Mg<sup>2+</sup>, Ni<sup>2+</sup>, Ca<sup>2+</sup>, Co<sup>2+</sup>). All cations are octahedrally coordinated, with Ca[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] as the only exception (CN = 8) crystallizing in an own structure type. There are two structure types for the “cation within layer” variant, namely Zn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] and Mn[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] differing merely in the orientation of one (SO<sub>4</sub>)-tetrahedron. The “cation between layer” compounds crystallize in the α-Mg[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] structure type. Polymorphism between these two variants is reported for M[B<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>] (M = Mg<sup>2+</sup>, Co<sup>2+</sup>).<sup>15,17,18</sup> Moreover, H[B(SO<sub>4</sub>)(S<sub>2</sub>O<sub>7</sub>)] is the only acid with reported crystal structure in the material class of borosulfates, so far.<sup>11</sup> In general, borosulfates can be considered to be salts of the superacid HB(HSO<sub>4</sub>)<sub>4</sub>.<sup>32</sup>

Herein, we present the syntheses and crystal structures of two novel phyllosilicate-analogous borosulfates, namely the

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heteropolyacid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  and the homeotypic  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ . The latter was postulated by Schott and Kibbel as early as 1962 based on gravimetry and acidimetric titration.<sup>33</sup> Herein, this compound's crystal structure and its optical and thermal properties are addressed. Coevally, a more detailed study of the complex thermal decomposition behaviour of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  is reported along with the two unconventional borosulfates  $\text{Cd}[\text{B}_2\text{O}(\text{SO}_4)_3]$  and  $\text{Cd}_4[\text{B}_2\text{O}(\text{SO}_4)_6]$ .

## Results and discussion

### Syntheses

Both compounds were prepared solvothermally.

$\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  was synthesized starting from  $\text{H}_3\text{BO}_3$  and liquid  $\text{SO}_3$ . For the exact titration of the latter, a specially designed apparatus is needed. It is detailed in the Experimental section. The starting materials were filled into a glass ampoule, which was subsequently sealed under reduced pressure and heat treated at 390 K. A white solid including several colourless single crystals was obtained (Fig. S1†). The utilization of the specially designed apparatus and titration of the exact amount of  $\text{SO}_3$  (0.4 ml for 200 mg  $\text{H}_3\text{BO}_3$ ) appears to be crucial for the successful synthesis. By lowering the amount of  $\text{SO}_3$  by only 0.1 ml, a colourless and highly viscous liquid is obtained, what we were able to show reproducibly (Fig. S2†). The liquid cannot be crystallized at reduced temperature. Crystals of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  are extremely hygroscopic. Furthermore, the solid sample reacts easily with a polyacetate foil (Fig. S3†). Consequently, no characterization beyond single-crystal XRD could be performed.

$\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  can be obtained *via* two different synthetic routes (I and II), both employing solvothermal syntheses starting from  $\text{CdO}$ ,  $\text{H}_3\text{BO}_3$  or  $\text{B}_2\text{O}_3$  and oleum (65%  $\text{SO}_3$ ). The starting materials were filled into glass ampoules, which were subsequently sealed, and heat treated at 523 K and 573 K, respectively. *Via* both routes, colourless powders containing large single crystals were obtained (Fig. S4†). Phase-purity was confirmed by powder X-ray (PXRD) diffraction and Rietveld refinement in both cases (Fig. S5, S6 and Table S1†). Noteworthy, no indication for synthesis dependent polymorphism was observed during these syntheses despite synthesis variations such as furnace temperature,  $\text{SO}_3$  content and aging – in contrast to the other transition metal borosulfates discussed in the Introduction.

### Crystal structures

$\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ . The heteropolyacid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  crystallizes in a new structure type in the triclinic crystal system with space group  $P\bar{1}$  (no. 2) and two formula units per unit cell (Fig. 1). Crystallographic details, bond lengths and angles can be found in Tables S2–S7.† The asymmetric unit of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  consists of four crystallographically independent  $(\text{SO}_4)$ - and two  $(\text{BO}_4)$ -tetrahedra (Fig. S7†). These are connected *via* common corners with alternating B–O–S bonds. All  $(\text{BO}_4)$ -tetrahedra share four vertices with one  $(\text{SO}_4)$ -tetrahedron. They

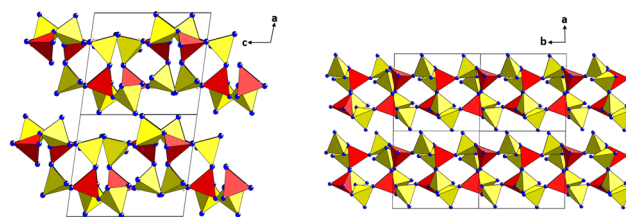


Fig. 1 Phyllosilicate analogue topology in the structure of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ . Hydrogen bonding occurs only within the layers and not in between the layers. Left: quadruple cell parallel to the crystallographic *b*-axis; right: quadruple parallel to the crystallographic *c*-axis; red tetrahedra –  $(\text{BO}_4)$ , yellow tetrahedra –  $(\text{SO}_4)$ .

form phyllosilicate-analogous layers comprising zwölf- and vierer rings and resembling the structural motive introduced before (Fig. 1 and 2). Two of the  $(\text{SO}_4)$ -tetrahedra exhibit significantly elongated terminal S–O bonds (S1–O1 149.78(8) and S3–O10 149.69(7) pm) which carry the hydrogen atoms, countering the charge of the heteropolyanion. From a strict ionic point of view, the crystal structure can be considered to consist of the borosulfate anion charge balanced by protons. Strong to moderately strong intra-layer hydrogen bonds are formed to adjacent  $(\text{SO}_4)$ -tetrahedra with donor–acceptor distances of 249.1(1) and 250.1(1) pm (Table S7†).<sup>35</sup> These may be considered a major cause for the distortion of the zwölf rings in

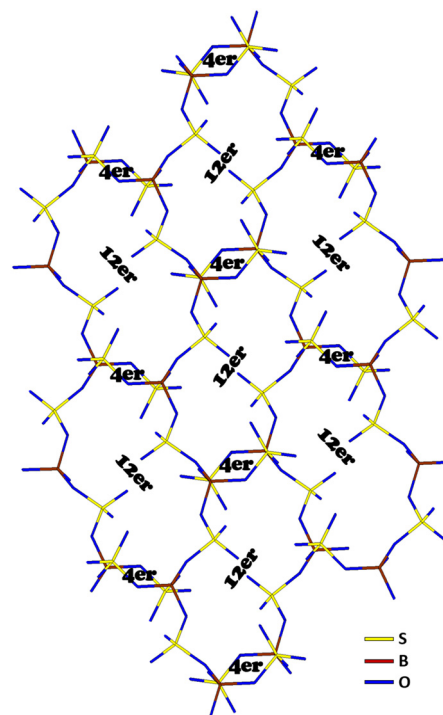


Fig. 2 Cut-out of the layers found for the structure of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  depicted in a wire and sticks model. Hydrogen atoms and respective bonds are omitted. The structure exhibits zwölf- and vierer-rings (abbreviated as 12er and 4er) of corner-linked  $(\text{SO}_4)$ - and  $(\text{BO}_4)$ -tetrahedra.



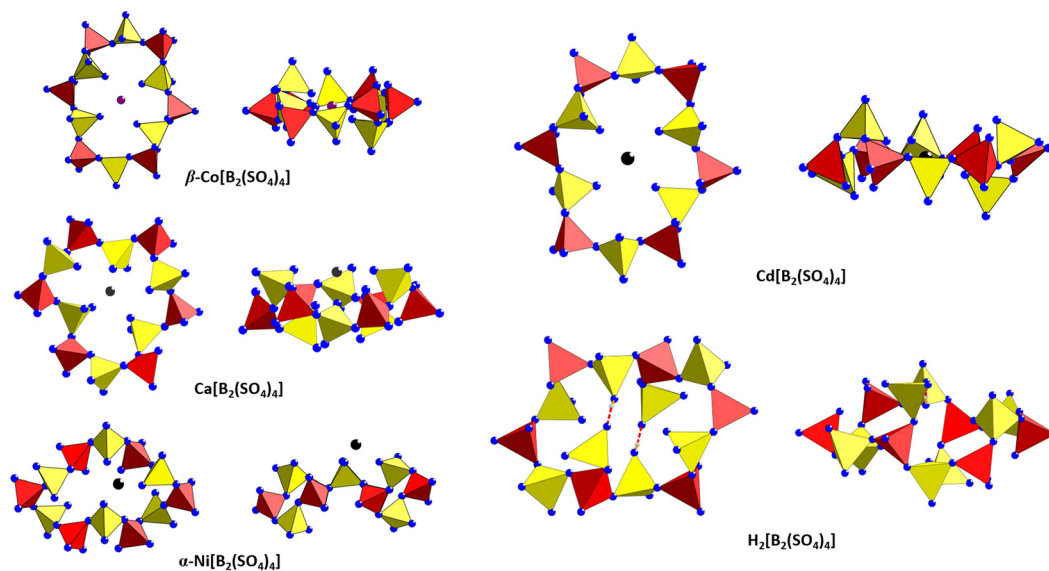


Fig. 3 Location of the cations in the structures of phyllosilicate-analogous borosulfates; red tetrahedra –  $(\text{BO}_4)$ , yellow tetrahedra –  $(\text{SO}_4)$ .

contrast to the homeotypic transition metal borosulfates (Fig. 3). Consequently, the stacking of the layers occurs only *via* van der Waals interactions.

The deviations from tetrahedral symmetry were calculated using the method of Balić-Zunić and Makovicky based on all ligands enclosing spheres on experimental data.<sup>36,37</sup> All  $(\text{BO}_4)$ - and  $(\text{SO}_4)$ -tetrahedra can be considered regular<sup>38</sup> with deviations between 0.2% and 0.3%.

**$\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ .**  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  crystallizes in the  $\text{Mn}[\text{B}_2(\text{SO}_4)_4]$  structure type<sup>30</sup> in the monoclinic crystal system with space group  $P2_1/n$  (no. 14) and two formula units per unit cell (Fig. 4 and S8†). Crystallographic details, bond lengths and angles can be found in Tables S8–S13 and Fig. S8.† As for  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , the borosulfate anion of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  forms  $\text{B}(\text{SO}_4)_4$  supertetrahedra exhibiting exclusively alternating B–O–S bonds. The supertetrahedra share alternately edges and corners forming sechser rings (Fig. S9†). Consequently, the anion can be classified as phyllosilicate-analogous. More precisely, the anion can be described by the Niggli formula  ${}^2_0\{[\text{B}(\text{SO}_4)_{2/2}{}^e(\text{SO}_4)_{2/2}{}^c]^{-}\}$  ( $e$  = edge sharing,  $c$  = corner sharing)

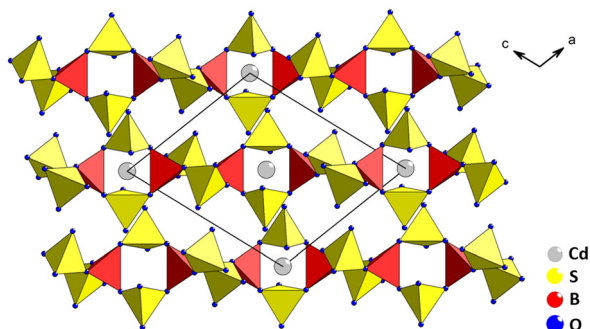


Fig. 4 Unit cell of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  viewed along  $[010]$ .

by considering the supertetrahedron  $\text{B}(\text{SO}_4)_4$  as building unit. Regarding the individual tetrahedra, the layers comprise zwölf and vierer rings. Each zwölf ring is connected to four other zwölf rings directly and to another two *via* vierer rings. The silicate-analogy can be demonstrated by the comparison to the mineral manganpyrosomalite comprising an anionic substructure formed by zwölf and vierer rings as well as additional sechser rings.<sup>39</sup> So far, no anion exhibiting exclusively zwölf and vierer rings has been observed for the class of silicates. The cadmium cation in  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  is octahedrally coordinated by six oxygen atoms, *i.e.* monodentately by six  $(\text{SO}_4)$ -tetrahedra (Fig. 5). Four  $(\text{SO}_4)$ -tetrahedra belong to an anionic layer with the cation residing inside the zwölf ring whereas the remaining two belong to the layers above and below, respectively.

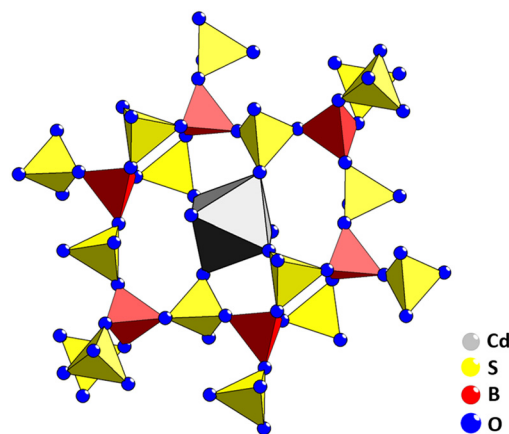


Fig. 5 Octahedral coordination environment of the cadmium cations in  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  and the location in the zwölf ring; the two additional oxygen atoms belong to the anion layers above and below, respectively.



In contrast to  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , the asymmetric unit of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  comprises only two crystallographically independent  $(\text{SO}_4)$ -tetrahedra and one  $(\text{BO}_4)$ -tetrahedron as well as one  $\text{CdO}_6$  octahedron (Fig. S8†). According to calculations by the method of Balić-Zunić and Makovicky, the  $(\text{BO}_4)$ - and  $(\text{SO}_4)$ -tetrahedra can all be classified as regular with deviations from the tetrahedral symmetry of 0.5%, 0.1% and 0.6% for  $\text{B}_1\text{O}_4$ ,  $\text{S}_1\text{O}_4$  and  $\text{S}_2\text{O}_4$ , respectively. The Cd–O distances ranging from 222.9(3) to 230.0(2) pm are reasonably close to the sum of ionic radii (220 pm).<sup>40</sup> The deviation from the octahedral symmetry amounts to 6.1%. This value differs insignificantly from isotypic  $\text{Mn}[\text{B}_2(\text{SO}_4)_4]$  ( $\Delta_{\text{octa}} = 7.9\%$ ) or homeotypic  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  ( $\Delta_{\text{octa}} = 5.8\%$ ).

On a more general note,  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  crystallizes in the  $\text{Mn}[\text{B}_2(\text{SO}_4)_4]$  structure type. As introduced before, there is the homeotypic  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  structure type also exhibiting “cations within layer” configuration (Fig. 3). The latter is also adapted by  $\beta\text{-Mg}[\text{B}_2(\text{SO}_4)_4]$ ,  $\beta\text{-Co}[\text{B}_2(\text{SO}_4)_4]$  and  $\beta\text{-Ni}[\text{B}_2(\text{SO}_4)_4]$ ,<sup>41</sup> while the only further example for the former structure type is  $\beta\text{-Cu}[\text{B}_2(\text{SO}_4)_4]$ . A trend can be found by comparing the acidity of the respective binary oxides. According to the Lux–Flood concept, these borosulfates can be considered to be combinations of the strong acids  $\text{SO}_3$  and  $\text{B}_2\text{O}_3$  and the basic transition metal oxides (*i.e.*  $\text{CdO}$ ,  $\text{MnO}$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{CuO}$ ).<sup>42</sup> When excluding the copper representative due to the dominant Jahn–Teller distortion in this compound, the  $\text{Mn}[\text{B}_2(\text{SO}_4)_4]$  structure type appears to be adapted for the stronger bases  $\text{MnO}$  and  $\text{CdO}$ , while the  $\text{Zn}[\text{B}_2(\text{SO}_4)_4]$  structure type is adapted for the slightly weaker remaining bases. Remarkably, polymorphism with “cation between layer” and “cation within layer” polymorphs was only observed by experiment for the latter structure type, so far.

### Crystallographic relationship

Chemically,  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  can be considered the metal salt of the heteropolyacid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ . This and the topological relationship is obvious when comparing the sum formulae and the layers consisting of zwölf and vierer rings (Fig. 3). Moreover,  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  may be considered as the free acid form of all the phyllosilicate-analogous transition metal borosulfates. Although both space groups as well as the unit cell sizes suggest a direct group–subgroup relationship of index 2 according to a Bärnighausen scheme, the distortion of both crystal structures, *i.e.* of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  and  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , with respect to each other is too significant to be subject to such a close relationship – an essence of the respective distortions of the anion despite the same topology is shown in Fig. S10.†

### Electrostatic calculations and continuous shape measures

The electrostatic reasonability of the crystal structures of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  and  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  and all coordination numbers were confirmed by calculations based on the MAPLE (MAdelung Part of Lattice Energy) concept (Tables S14†).<sup>43–46</sup> These calculations yielded analogous effective coordination numbers for  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  as for the isotypic and homeotypic compounds (Tables S15 and S16†).

In Table S17† the Continuous Shape Measure (CShM) values<sup>47</sup> for the coordination polyhedra of the non-oxygen atoms within the asymmetric units of all currently known phyllosilicate-analogous borosulfates are summarized. The CShM values were calculated using the algorithm developed by Casanova *et al.* using the Shape 2.1 program.<sup>48</sup>

### Hirshfeld-surface analysis

In order to visualize the non-covalent interactions (NCIs) within the network of the free acid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , Hirshfeld-surfaces and fingerprint plots are utilized.<sup>49,50</sup> The Hirshfeld-surface is the isosurface where the ratio of the spherically averaged electron densities of atoms inside the surface (the promolecule) and all atoms in the structure is equal to 0.5.<sup>49</sup> Two values, the distances to the closest atom on the interior ( $d_i$ ) and the exterior ( $d_e$ ), are associated to every point on the surface. In this work, we exclusively show  $d_{\text{norm}}$  mapped onto the surfaces, which is given by:

$$d_{\text{norm}} = \frac{(d_i - r_i^{\text{vdW}})}{r_i^{\text{vdW}}} + \frac{(d_e - r_e^{\text{vdW}})}{r_e^{\text{vdW}}}$$

where  $r_i^{\text{vdW}}$  and  $r_e^{\text{vdW}}$  are the van der Waals-radii of the respective atoms. The surface is then coloured with a gradient from red (negative  $d_{\text{norm}}$  values, *i.e.* close contacts) over white ( $d_{\text{norm}}$  is equal to zero, *i.e.* exact van der Waals-radii) to blue (positive  $d_{\text{norm}}$  values, weak interactions). The fingerprint plots are a scatterplot of  $d_e$  vs.  $d_i$  for all points on a Hirshfeld-surface and may be used to identify strong interactions as spikes directed to the origin of the plot.

The Hirshfeld-surface around one zwölf ring displays – in line with the crystal structure description before – the lack of strong interactions between the layers (Fig. S11 and S12†). Any hydrogen bonding is strictly confined to the inside of the layer and accounts for 22.9% of the surface of one zwölf ring (Fig. 6). The associated fingerprint plot displays three distinct spikes corresponding to the O–B and O–S contacts (covalent bonds) within the layers as well as the donor/acceptor-pairs of the hydrogen bridges within the layers. The large green area in the full fingerprint plot corresponds to the van der Waals contacts of the zwölf ring to the adjacent layers.

The morphology and mapping on the Hirshfeld-surfaces around the two hydrogen atoms in the structure shows that the hydrogen bridges occur exclusively within the same layer (Fig. 7). This is in contrast to all hitherto known phyllosilicate-analogous borosulfates. There, the cations inside the rings are always coordinated by oxygen atoms of the adjacent layers – either two or three layers contribute to the cation’s coordination in the “cation between layers” and “cation within layers” configurations, respectively. This lack of inter-layer bonding might explain the observed extraordinary reactivity of the compound.

### Optical properties

**Infrared spectroscopy.** The infrared spectrum of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  is shown in Fig. S13.† The spectrum resembles those of isotypic  $\beta\text{-Cu}[\text{B}_2(\text{SO}_4)_4]$ , homeotypic  $\alpha\text{-Co}[\text{B}_2(\text{SO}_4)_4]$





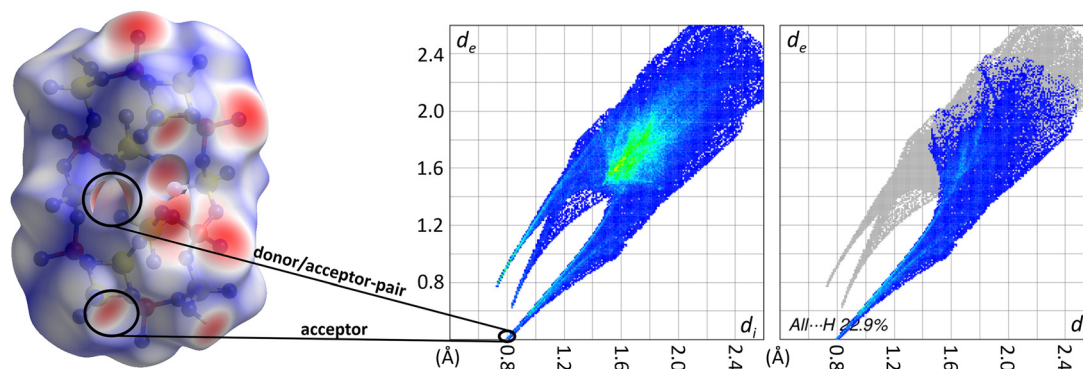


Fig. 6 Hirshfeld-surface mapped with  $d_{\text{norm}}$  around one zwölfer ring viewed along the stacking direction in the structure of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  (left, the same excerpt is shown in Fig. 7 left). Full fingerprint plot of the surface (top-right) and fingerprint plot delineated into the contacts to exterior H-atoms (bottom-right) contributing to 22.9% of the surface area.

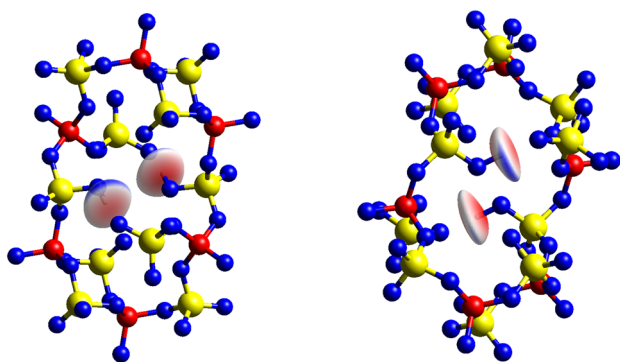


Fig. 7 Hirshfeld-surfaces mapped with  $d_{\text{norm}}$  around both crystallographically independent H-atom positions inside their respective ring structures H1 on the left and H2 on the right; blue – oxygen, red – boron, yellow – sulfur.

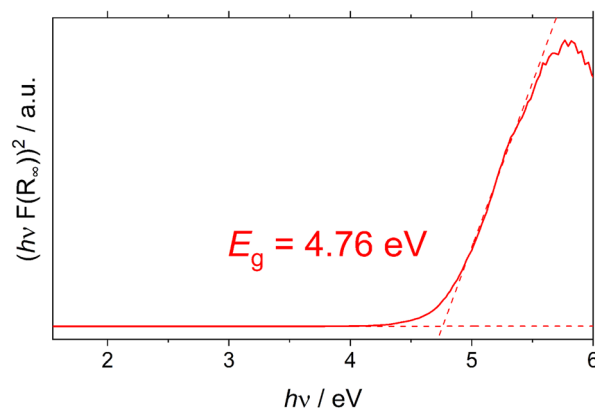


Fig. 8 Tauc plot calculated from the UV-Vis spectrum of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  shown in Fig. S14† assuming a direct band gap.

and  $\beta\text{-Mg}[\text{B}_2(\text{SO}_4)_4]$ . The S–O stretching modes appear between  $1400$  and  $1300\text{ cm}^{-1}$  and around  $1200\text{ cm}^{-1}$ . The subsequent bands between  $1180\text{ cm}^{-1}$  and  $850\text{ cm}^{-1}$  can be assigned to  $\nu_{\text{asym/sym}}$  (B–O) and  $\nu_{\text{sym}}$  (S–O). Below, the spectrum is governed by bending vibrations, namely the asymmetric bending vibrations  $\delta_{\text{asym}}$  (O–S–O, O–B–O, S–O–B) between  $720\text{ cm}^{-1}$  and  $435\text{ cm}^{-1}$  and  $\delta_{\text{asym}}$  (O–S–O, S–O–Cd) below.

**UV-Vis spectroscopy.** The powder reflectance spectrum of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  is shown in Fig. S14.† It is governed by the fundamental absorption due to the bandgap of the sample in the UV regime since there are no valence d electrons in  $\text{Cd}^{2+}$ . The optical band gap was estimated using the Tauc plot in Fig. 8 with an experimental value of  $4.76(1)\text{ eV}$ .

### Thermal analysis

The thermal decomposition of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere and temperature-programmed powder X-ray diffraction (TPXRD) inside a sealed argon filled glass capillary. According to the results of the former (Fig. 9),  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  decomposes above  $330\text{ }^\circ\text{C}$  via a two-step process. After the first step, amor-

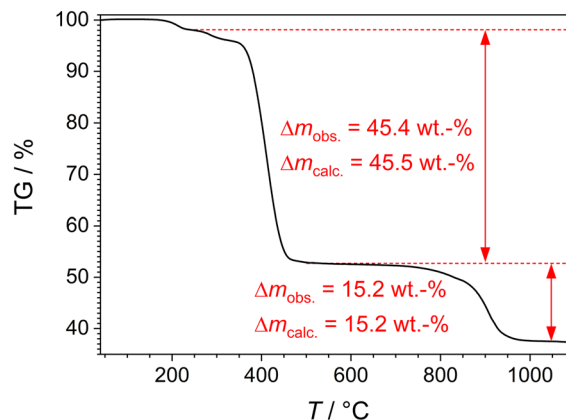
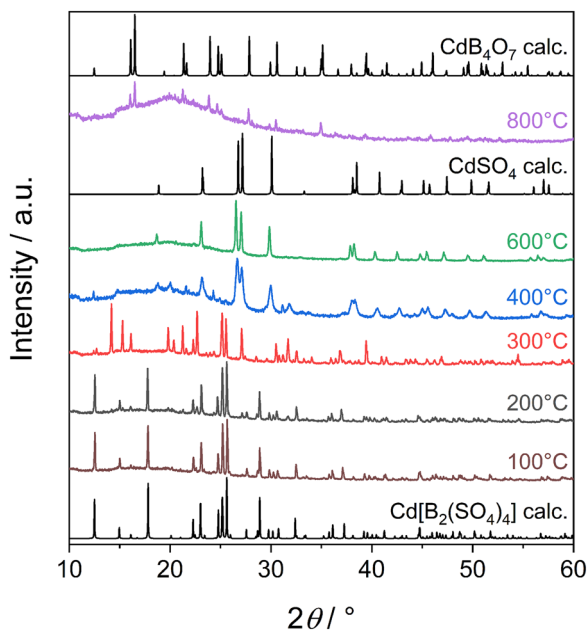


Fig. 9 Thermogravimetric analysis of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ : prior to the decomposition of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ , adhesive sulfuric acid evaporates resulting in the small step below  $300\text{ }^\circ\text{C}$ .

phous  $\text{B}_2\text{O}_3$  and  $\text{CdSO}_4$  are formed. In turn, the latter decomposes starting at  $850\text{ }^\circ\text{C}$  to  $\text{CdO}$ . These steps are accompanied by the evaporation of three moles  $\text{SO}_3$  and one  $\text{SO}_3$ , respect-





**Fig. 10** TPXRD patterns of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  compared to calculated patterns for  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  from SC-XRD,  $\text{CdSO}_4$ <sup>54</sup> and  $\text{CdB}_4\text{O}_7$ <sup>55</sup> details are discussed in the text.

ively. The last step is in accordance with earlier reports on the thermal decomposition of  $\text{CdSO}_4$ .<sup>51</sup> Additionally, the decomposition process was investigated by TPXRD (Fig. 10) confirming the formation of  $\text{CdSO}_4$  and showing the formation of  $\text{CdB}_4\text{O}_7$  at 800 °C – by the reaction of  $\text{CdO}$  and  $\text{B}_2\text{O}_3$ . This behaviour is well-known for borosulfates.<sup>15,52</sup> Gravimetrically, it is not possible to discriminate between mixtures of  $\text{CdO}$  and  $\text{B}_2\text{O}_3$ , and of  $\text{CdO}$  and  $\text{CdB}_4\text{O}_7$ . Measurements at higher temperatures close to the melting point of  $\text{CdB}_4\text{O}_7$  (976 °C)<sup>53</sup> resulted in a loss of crystallinity presumably accompanied by glass formation. This also explains why no PXRD could be measured using the residue from the TGA measurement. Additionally, a sample of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  heated for 10 h at 1000 °C in a corundum crucible inside a tube furnace could not be separated from the crucible after the heat treatment – presumably due to the same reason. Interestingly, a novel pattern was observed at 300 °C (Fig. 10). This is related to the formation of simultaneously reported  $\text{Cd}[\text{B}_2\text{O}(\text{SO}_4)_3]$ .<sup>34</sup> A more detailed description of the complex thermal decomposition of these cadmium borosulfates is given in the respective publication.

## Experimental section

### Syntheses

**$\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ .** To synthesize  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , the generation of  $\text{SO}_3$  is essential. However,  $\text{SO}_3$  is an extreme oxidizer and needs careful handling. Furthermore, it is very moisture sensitive. Thus, we used a specially designed glass apparatus and procedure that allows for a reaction under complete exclusion of air.

To synthesize the acid,  $\text{H}_3\text{BO}_3$  (200 mg, Carl Roth, 99.8%) was placed a thick-walled glass ampoule (length 300 mm, outer diameter 16 mm, wall thickness 1.8 mm) and attached to an apparatus for the generation of  $\text{SO}_3$ . The latter has been conducted under strictly inert atmosphere. To generate  $\text{SO}_3$ , oleum (Sigma-Aldrich, 20%  $\text{SO}_3$ ) was added carefully to an excessive amount  $\text{P}_4\text{O}_{10}$  (Merck, 97%). In the following, the mixture was heated to 130 °C *via* an oil bath. Thus,  $\text{SO}_3$  was transferred to the gaseous phase. Above the dropping funnel a Teflon®-lined manometer has been used to monitor the pressure.  $\text{SO}_3$  accumulates in a burette, which is part of the specially designed apparatus. The burette is accessible after opening a Teflon®-lined valve. Eventually, liquid  $\text{SO}_3$  has been added dropwise to the attached ampoule *via* utilization of the burette. For the synthesis of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  an amount of 0.4 ml  $\text{SO}_3$  is needed. Additionally, the ampoule was torch sealed under reduced pressure and placed in a box furnace. The ampoule was heated to 393 K from 298 K with a heating rate of 0.07 K min<sup>-1</sup>. The temperature was maintained for 48 h and finally reduced to 298 K with a cooling rate of 0.02 K min<sup>-1</sup>.

**$\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ .** *Via* synthesis I, 86.1 mg  $\text{CdO}$  (Fluka, 99%), 300 mg  $\text{H}_3\text{BO}_3$  (Carl Roth, 99.8%) and 1 ml oleum (Sigma-Aldrich, 65%  $\text{SO}_3$ ) were loaded into a thick-walled glass ampoule (length 300 mm, outer diameter 16 mm, wall thickness 1.8 mm). The ampoule was torch-sealed under reduced pressure and placed in a box furnace. The ampoule was heated to 523 K from 298 K with a heating rate of 1.67 K min<sup>-1</sup>. The temperature was maintained for 96 h and eventually reduced to 298 K with a cooling rate of 0.04 K min<sup>-1</sup>.

For synthesis II, 0.5 mmol  $\text{CdO}$  (Fluka, 99%) and 1.25 mmol  $\text{B}_2\text{O}_3$  (Sigma-Aldrich, 99%) were ground together, and loaded into a silica glass ampoule (length 150 mm, outer diameter: 12 mm, wall thickness: 1 mm) together with 1 ml oleum (VWR, 65%  $\text{SO}_3$ ). Subsequently, the ampoule was fused under ambient pressure and placed in a muffle furnace applying the following temperature program: heating to 573 K with a heating rate of 100 K h<sup>-1</sup>, holding the temperature for 60 h, and cooling down to room temperature with a cooling rate of 100 K h<sup>-1</sup>.

The ampoules were opened after cooling with liquid nitrogen (**Caution:** During and even after the reaction the ampoules are under remarkable pressure and must therefore be handled with care). After decantation of the excess sulfuric acid, the Entweder weglassen oder Summenformel samples were washed with 5 ml anhydrous acetonitrile (Acros, 99.9%, extra dry) using a frit in a Schlenk line under nitrogen atmosphere. Afterwards, the product were transferred into an argon filled glovebox. The product is sensitive towards moisture and hence was stored under inert conditions for further investigations. Even minimal quantities of  $\text{H}_2\text{O}$  lead to the degradation of  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  towards  $\text{CdSO}_4 \cdot \text{H}_2\text{O}$  (Fig. S15†).

### Single-crystal structure determination

Immediately after opening the ampoules, single-crystals were taken directly out of the mother liquor and transferred into inert oil. Suitable single-crystals were selected under a polarizing microscope, mounted onto a glass needle ( $\varnothing = 100 \mu\text{m}$ ) or



a MicroLoop (MiTeGen,  $\varnothing = 50 \mu\text{m}$ ) and immediately placed into a stream of cold nitrogen inside the diffractometer. Diffraction data were collected with Bruker D8 Quest  $\kappa$  and Bruker D8 Venture diffractometers using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption correction was performed by the multi-scan method. The structures were solved by direct methods difference Fourier techniques and refined by full-matrix least-squares technique with the SHELXL crystallographic software package.<sup>56</sup> Anisotropic refinement was performed for all non-hydrogen atoms. The hydrogen atoms were refined freely using residual density of electrons for localization. Relevant crystallographic data and further details of the structure determinations are summarized in Tables S2 and 13.†

Further details of the crystal structure investigations may be obtained at <https://www.ccdc.cam.ac.uk/> on quoting the depository numbers CCDC-2207483 ( $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ ), CCDC-2176209, CCDC-2171676 ( $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ ), the names of the authors, and citation of this publication. CCDC-2176209 gives the data measured at 173(2) K, whereas CCDC-2171676 gives the data for a measurement at 250(2) K. The latter was also used for the discussion in the main manuscript, if not stated otherwise.

### X-ray powder diffraction

The samples were ground and filled into glass capillaries (outer diameter 0.7 mm or 0.3 mm, wall thickness 0.01 mm) inside an argon filled glovebox. The data were collected – both in transmission geometry – with a Stoe Stadi P powder diffractometer with Ge(111)-monochromatized Mo- $K_{\alpha 1}$ -radiation ( $\lambda = 0.7093 \text{ \AA}$ ) and a Dectris Mythen 1K detector, and Bruker D8 Advance diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with a 1D LynxEye detector, steps of  $0.02^\circ$ , generator driven at 40 kV and 40 mA, respectively. For the latter instrument, the higher background at lower diffraction angles is due to the absorption of the glass capillary.

Temperature-programmed X-Ray powder diffraction (TPXRD) was performed with the latter device using a furnace attachment and a silica-glass Hilgenberg capillary (outer diameter 0.3 mm, wall thickness 0.01 mm). The additional background between  $12.5^\circ < 2\theta < 30^\circ$  is due to the used furnace attachment.

### Rietveld refinement

Analysis of diffraction data was performed using the Rietveld method with the programs Topas 4.2<sup>57</sup> and TOPAS 5,<sup>58</sup> respectively. The instrumental resolution function was determined empirically from a set of fundamental parameters using a reference scan of Si (NIST 640d).<sup>59</sup> The structural model from our single-crystal XRD measurement was used as a starting model for Rietveld analysis. The isotropic displacement parameters were constrained to one common value for all atoms in order to minimize quantification errors. Details are displayed in Fig. S5 and S6 as well as Table S1.†

### Hirshfeld-surface analysis

To calculate the Hirshfeld-surfaces, the CrystalExplorer 21.2<sup>50</sup> program-package was used. All hydrogen bonds lengths were set to normalized values ( $0.983 \text{ \AA}$  for O–H) by the program

prior to the calculation. The electron densities for each atom type were taken from the basis sets calculated by Koga *et al.*<sup>60</sup> and the surfaces were generated on the very high setting for the number of grid points.

### FTIR spectroscopy

The ground sample was mixed with KBr in a roughly 1:10 ratio and pressed with a pressure apparatus with a set pressure of 0.6 tons. The thin and slightly transparent pellet was placed into a BRUKER Alpha II FT-IR-Spectrometer. Scans were performed in a range from  $360 \text{ cm}^{-1}$  to  $4000 \text{ cm}^{-1}$ , with a resolution of  $2 \text{ cm}^{-1}$  and 90 scans per sample. Background corrections were applied by measuring a pure KBr pellet. The used program was Opus version 8.<sup>61</sup>

### UV-Vis spectroscopy

The UV-Vis spectrum was recorded as diffuse reflection spectrum at room temperature with a Varian Cary 300 Scan UV-Vis spectrophotometer using an Ulbricht sphere detector and a deuterium lamp/tungsten-halogen lamp light source (scan range: 200–800 nm, increment 1 nm, scan rate:  $120 \text{ nm min}^{-1}$ ).

### Thermal analysis

The thermogravimetric analysis (TGA) was performed with a NETZSCH STA 409 PC Luxx thermobalance under nitrogen atmosphere with  $70 \text{ mL min}^{-1}$  flow in alumina crucibles (heating rate:  $10 \text{ K min}^{-1}$ ).

## Conclusions

Multiple transition metal borosulfates with the general sum formula  $\text{M}[\text{B}_2(\text{SO}_4)_4]$  are known comprising phyllosilicate-analogous anionic substructures formed by adjacent zwölf- and vierer rings. In this contribution, the “parent” acid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  is presented and another member, namely  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ , is added to the aforementioned group. The hydrogen bonding situation in  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  occurs solely within the zwölf rings, *i.e.* within the borosulfate layer. This and the resulting distortion of these rings could be described in detail by Hirshfeld-surface analysis.  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  can be described as the cadmium salt of the heteropolyacid  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ . It adapts the  $\text{Mn}[\text{B}_2(\text{SO}_4)_4]$  structure type with “cation within layers” configuration. Further, the optical properties investigated by infrared and UV-Vis spectroscopy are in line with the X-ray diffraction results and revealed an optical band gap of 4.76 eV using a Tauc plot. Thermally,  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$  decomposes at  $330 \text{ }^\circ\text{C}$  *via* a two-step process to CdO and  $\text{B}_2\text{O}_3$ . In future experiments, we will elucidate if the acid can be used directly to synthesize the respective phyllosilicate-analogous metal borosulfates.

## Author contributions

M. H. prepared  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ , solved its crystal structure and did the characterization by UV-Vis spectroscopy and the thermal analysis, and wrote parts of the original



draft. L. C. P. independently prepared  $\text{Cd}[\text{B}_2(\text{SO}_4)_4]$ , solved its crystal structure and did the characterization *via* IR spectroscopy, and wrote parts of the original draft. S. S. did the experiments on  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$ , conducted the Hirshfeld analysis and wrote parts of the original draft. H. H. and J. B. supervised the work by L. C. P., H. A. H. supervised the work by M. H. and wrote parts of the original draft. J. B. supervised the work by S. S., prepared the first sample of  $\text{H}_2[\text{B}_2(\text{SO}_4)_4]$  and wrote parts of the original draft. All authors reviewed and edited the final draft of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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