The First Borosulfate $K_5[B(SO_4)_4]$

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Sulfate anions SO_4^{2-} do not show a strong tendency to form condensed oligoanions owing to the high formal charge of sulfur. A recent very interesting example for an oligosulfate is $ReO_2Cl(S_2O_7)$.[1] Disulfate tetrahedra share common corners with an adjacent ReO_6 octahedron forming a cyclic moiety. Regarding oligosulfates, only chainlike anions, typically $S_3O_{10}^{2-}$ or even $S_5O_{16}^{2-}$, were described.[2–5] In $K_5[B(SO_4)_4]$, sulfate tetrahedra avoid direct condensation but form the unprecedented anion $[B(SO_4)_4]^{5-}$ shown in Figure 1. In nature, the same topology is only found in the mineral Zunyite, which formally contains the open-branched silicate anion $[Si(SiO_4)_4]^{12-}$. This silicate anion obeys T_d symmetry[6,7] and is connected to AlO_6 octahedra forming an alumosilicate network structure. In contrast, the $[B(SO_4)_4]^{5-}$ anions in potassium borosulfate are not covalently bound to other species and thus form non-condensed units.

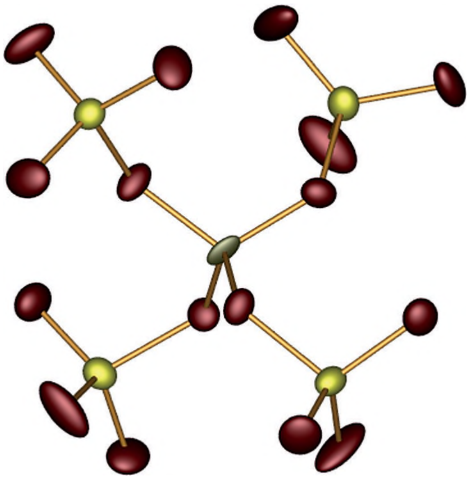

Figure 1. The borosulfate anion in $K_5[B(SO_4)_4]$ (B gray, S yellow, O red). Thermal ellipsoids are set to 50% probability.

To the best of our knowledge, there is no example for such an anion topology in sulfate and phosphate chemistry. Oligophosphates are restricted to form linear anions, as observed in Trömelite $Ca_4[P_6O_{19}]$,[8] but the borophosphates $M_6[B(PO_4)_4][PO_4]$ (M = Pb, Sr) contain a topologically identical moiety, the $[B(PO_4)_4]$ anion.[9] Moreover, it is not common in structures at ambient pressure that all four apices of a borate tetrahedron are connected to adjacent tetrahedra. One of the rare examples is $Ba_3[BP_3O_{12}]$ in which open-branched building units $[B(PO_4)_4]$ are condensed by common phosphate tetrahedra.[10,11]

$K_5[B(SO_4)_4]$ crystallizes in a new structure type in the chiral space group $P4_1$. The crystal structure of $K_5[B(SO_4)_4]$ comprises novel, large non-condensed anions $[B(SO_4)_4]^{5-}$ in which a central borate tetrahedron shares all four corners with neighboring sulfate tetrahedra. These central boron atoms adopt an only slightly distorted body-centered packing with the apices of the borate tetrahedra pointing more or less directly along the c axis, resulting in a polar crystal structure. The potassium atoms are situated in the voids of the resulting structure (Figure 2).

As observed for phosphate or silicate chains, the bonds from phosphorus atoms to the bridging oxygen atoms O^{br} are significantly longer compared with those to the terminal oxygen atoms O^{term}, and this also holds for $K_5[B(SO_4)_4]$. The bond lengths $S-O^{term}$ range from 139 to 146 pm, and the bond

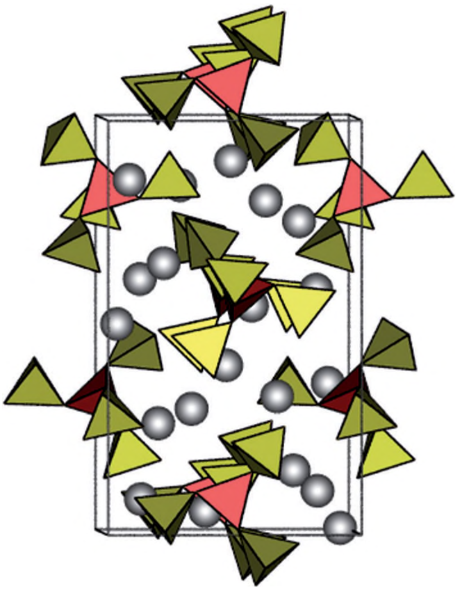

Figure 2. The unit cell of $K_5[B(SO_4)_4]$ (boron-centered tetrahedra red, sulfur-centered tetrahedra yellow, K gray) viewed approximately along [100].

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lengths S–O^{br} range from 154 to 157 pm. Within the BO_4 tetrahedron, the bond lengths lie between 145 and 148 pm. A good example to compare to our condensed anion is $[Si(S_2O_7)_3]$ in which the central silicon atom is sixfold-coordinated by three bidentate disulfate anions.[12] Therein the bridging S–O bonds to neighboring sulfate tetrahedra are significantly longer than those to the central silicon atom. These latter bonds are longer than the terminal S–O bonds, in accordance with our results.

An excellent measure for deviations of tetrahedra from the ideal symmetry is the method suggested by Balic-Žunic and Makovicky,[13,14] which we have already applied to poly- and cyclophosphates such as β-$Ln(PO_3)_3$ (Ln = Sc, Y, Tb…Yb) and $Ba_2(P_4O_{12})\cdot 3.5\,H_2O$.[15,16] For these we identified typical values for condensed phosphate tetrahedra of less than 1%. In the borosulfate anion, the deviations are well below this mark (BO_4: 0.43%, SO_4: 0.08–0.23%) and all of the tetrahedra may be classified as regular.

The potassium ions are coordinated only by terminal oxygen atoms of the borosulfate anions $[B(SO_4)_4]^{5-}$. K1 (CN = 7, av. 288 pm), K2 (CN = 11, 312 pm), K3 (CN = 8, 290 pm), K4 (CN = 7, 283 pm), K5 (CN = 9, 287 pm) are surrounded by oxygen atoms with distances between 266 and 350 pm. This distance range agrees very well with the sum of the ionic radii; that is, 286 (CN = 7) to 295 pm (CN = 9) for K^+–O^{2-}.[17] These coordination numbers were confirmed by MAPLE calculations yielding effective coordination numbers (Table 1).

Table 1: Results of the MAPLE calculation for $K_5(B[SO_4]_4)$ compared with the MAPLE calculations on chemically similar known compounds.

$K_5(B[SO_4]_4)$	$2\,K_2S_2O_7$[13] + $0.5\,K_2O$[14] + $0.5\,B_2O_3$[15]
MAPLE = 140112 kJ mol^{-1} (Δ=0.8%)	MAPLE = 138974 kJ mol^{-1}

We checked our structure model for electrostatic reasonability using calculations based on the MAPLE concept.[21–23] A structure model is electrostatically consistent if the sum of MAPLE values of chemically similar compounds deviates from the MAPLE value of the compound of interest by less than 1%. According to our calculations, the structure model of $K_5(B[SO_4]_4)$ thus shows electrostatic consistency, as presented in Table 1.

The synthesis starting from boric acid, potassium sulfate, and sulfuric acid yielded a phase-pure crystalline powder (Figure 3). The intensities and also the positions of all of the reflections are in very good agreement with the calculated values based on the previously described structure model derived from single-crystal data.

Figure 4 shows the IR and Raman spectra of $K_5[B(SO_4)_4]$. The characteristic bands of the tetrahedral BO_4 and SO_4 groups are observed between 1500 and 400 cm^{-1}.[24,25] In the IR spectrum, the very strong band at about 1200 cm^{-1} can be assigned to the ν_{as}(S–O) vibrations of the SO_4 tetrahedra. The characteristic peaks of the $\nu_{as}(BO_4)$ are in the region between 930 and 1090 cm^{-1}. The absorption from 660 cm^{-1} to 920 cm^{-1} is assigned to $\nu_s(BO_4)$. The bending modes ($\delta(SO_4)$) of sulfate occur at about 600 cm^{-1} and of borate ($\delta(BO_4)$) at about 570 cm^{-1}.[26] The symmetric S–O bending vibrations of the SO_4 tetrahedra appear in the 500–450 cm^{-1} region.

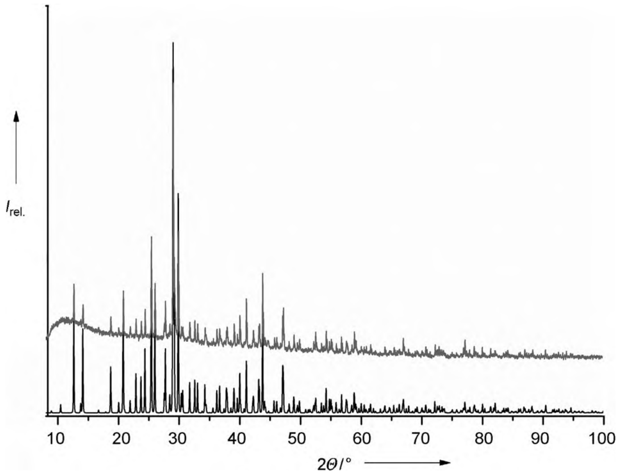

Figure 3. X-ray powder diffraction pattern of $K_5[B(SO_4)_4]$ (Cu $K_{\alpha 1}$ radiation) compared with a calculated pattern based on the structure model obtained from single-crystal data.

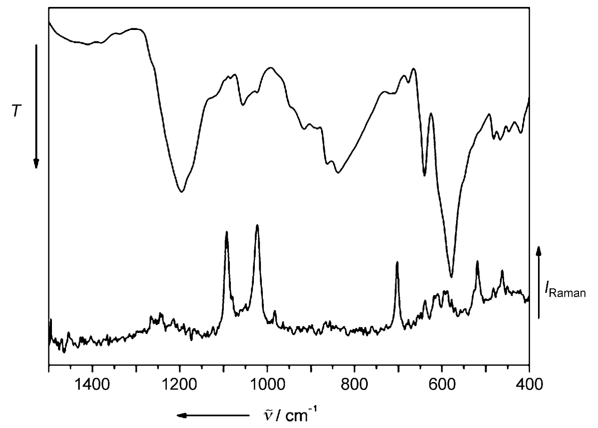

Figure 4. Vibrational spectra of $K_5[B(SO_4)_4]$. Top: IR spectrum, bottom: Raman spectrum.

All of the bands observed in the range from 1500 to 450 cm^{-1} in the Raman spectrum correspond to typical vibration modes of BO_4 and SO_4 groups. The sharp bands at 1090 cm^{-1} and 1020 cm^{-1} could be assigned to the bridging and terminal stretching vibrations of the SO_4 groups, respectively. The band at about 700 cm^{-1} can be attributed to the stretching vibration of the borate and sulfate tetrahedra. The bending modes of sulfate and borate tetrahedra were detected around 600 cm^{-1}. The symmetric S–O bending vibrations were observed near 450 cm^{-1}. No significant vibrations could be detected above 1500 cm^{-1}.

To confirm our assignment and to obtain force constants of the relevant bonds within the $(B[SO_4]_4)^{5-}$ anion, we performed a fit of the vibrations using the program VIBRATZ.[27] As expected, the terminal S–O bonds show the larger force constants (7.31 mdyn Å^{-1}) compared with the bridging S–O bonds (4.65 mdyn Å^{-1}); in disulfate anions

$S_2O_7^{2-}$, the terminal and bridging bonds exhibit rather similar force constants of 8.21 and 3.36 mdyn Å^{-1}, respectively.[28] The force constants of the B–O bonds are 3.55 mdyn Å^{-1} and thus in the same range as found for BO_4 tetrahedra in $[B(OH)_4]^-$ (3.52 mdyn Å^{-1}).[29] Accordingly, the observed frequencies in the spectra correspond very well with the expected values and our structure model. Detailed band-structure calculations on borosulfates are planned for the future.

Experimental Section

Synthesis of $K_5(B[SO_4]_4)$: Initially, K_2SO_4 (564 mg, 3.24 mmol, Aldrich, $\geq 99\%$) was dissolved in H_2O (8 mL). This solution was added to a mixture containing $B(OH)_3$ (200 mg, 3.22 mmol, Merck, $\geq 98\%$) dissolved in conc. H_2SO_4 (10 mL) and transferred to a porcelain crucible. The reaction was completed under air by applying the following temperature program: heating up to 510 K with a rate of 90 K h^{-1}, holding this temperature for 6 h, raising to 730 K within 2 h, holding this temperature for 12 h, before cooling to room temperature at a rate of 30 K h^{-1}. We obtained 743 mg (97 % yield) of the crystalline, colorless, and slightly hygroscopic product. The phase purity of the isolated sample of $K_5(B[SO_4]_4)$ was confirmed by powder X-ray diffraction (Figure 3).

Single-crystal X-ray diffraction data were collected on a Stoe IPDS 2 diffractometer. The data were corrected for absorption by applying a numerical correction on the basis of an optimized crystal shape by the program X-Shape (Stoe & Cie, Darmstadt, Germany). The crystal structure of $K_5(B[SO_4]_4)$ was solved by direct methods using the SHELXTL program package[30] in the polar tetragonal space group $P4_1$ (no. 76) and refined applying a twin law (01010000−1; BASF = 0.373(3)) with anisotropic displacement parameters for all atoms. Summary of the crystal data: Colorless block ($0.25 \times 0.22 \times 0.15$ mm^3), tetragonal, $P4_1$, $Z=4$, $a=990.23(5)$ pm, $c=1618.7(1)$ pm, $V=1587.2 \times 10^6$ pm^3, $\rho_{\text{x-ray}}=2.471$ g cm^{-3}, $2\theta_{\max}=50°$, $\lambda(\text{Mo K}_{\alpha1})=71.073$ pm, 298 K, 4139 reflections, 2735 unique reflections (2486 observed) ($R_{\text{int}}=0.042$, $R_s=0.054$), numerical absorption correction ($\mu=1.992$ mm^{-1}, min./max. transmission = 0.62/0.75, full-matrix least-square refinement (237 parameters) on F^2, Flack parameter −0.03(11), $R_1=0.053$, $wR_2=0.096$ for 2735 reflections and $R_1=0.047$, $wR_2=0.094$ for 2486 reflections with $I > 2\sigma(I)$, max./min. residual electron density = 0.36/−0.34 e$^-$/10^6 pm^3. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-424027.

Powder X-ray diffraction data were collected on a Bruker Advance D8 diffractometer using Cu-K$_{\alpha1}$ radiation at room temperature (LynxEye 1-D detector, with steps of 0.2°, acquisition time 900 s/step; Soller slits 4°, fixed divergence slit 1 mm, transmission geometry). The generator was driven at 40 kV, 40 mA. The observed intensities are in very good agreement with the calculated diffraction pattern based on the single crystal data (Figure 3).

Vibrational spectra of a phase-pure sample of $K_5(B[SO_4]_4)$ were collected at room temperature by using a Bruker EQUINOX 55 FTIR spectrometer. The Raman spectrum was recorded by a Bruker FRA 106/S module with a Nd-YAG laser ($\lambda = 1064$ nm) scanning a range from 400 to 4000 cm^{-1}.

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