Experimental Detail

The $K_2[B(AsO_3OH)_2]$ reaction mixture consisted of H_3BO_3 (0.4637g, 7.5mmol), $NH_4H_2AsO_4$ (1.1923g, 7.5mmol) and KCl (0.3728g, 5mmol), these were mixed in a pestle and mortar before being added to a 23mL Teflon-lined steel autoclave and heated to 513K for 240 h.. The product was washed with hot deionized water to dissolve the remaining borate flux, leaving colourless crystals of the desired phases as the only solid product (yield = 56%, based on As). This synthetic procedure was also used for the cesium chloride derivative; in this case CsCl (0.8418g, 5mmol) was used in place of potassium chloride producing $(Cs_2[BAsO_3OH]_8[AsO_4]_2[CsCl_4]Cl)_2$) in 63% yield.

A colourless crystal of (**I,** $K_2[B(AsO_3OH)_2]$) ($0.10 \times 0.10 \times 0.06$ mm^3) was selected for X-ray diffraction using a Bruker Nonius KappaCCD system at 120(2) K. The compound crystallised in the tetragonal space group $P4_32_12$ (no. 92) with a = 7.3568(5) Å and c = 15.4671(10) Å, V = 837.12(10)$Å^3$, Z = 4, ρ_{calcd} = 2.927gcm^{-3}. A total of 7469 reflections were collected by ϕ and ω scans in the range $2.91^o < \theta < 27.48^o$ using MoK_α radiation (λ = 0.71073Å), of which 1008 were unique. The structure was solved and refined by full-matrix least-squares on F^2 using the Patterson method with SHELX-97[17]. There were 61 parameters and the hydrogen atom was fixed at a calculated distance and refined in a riding mode. SADABS[18] was used to perform the absorption correction parameter refinement on 6891 reflections reduced R(int) from 0.0773 to 0.0426. Ratio of minimum to maximum apparent transmission: 0.577071. The given T_{min} (0.4435) and T_{max} (0.5839) were generated using the SHELX SIZE command. Lorentzian polarisation was corrected using scalepack[19].

The highest remaining peak 0.88, 1.85Å from H1. Final R1 value 0.0541 and wR 0.1579 for 962 independent reflections ($I > 2\sigma(I)$).

A colourless crystal of (**II**, $(Cs_2[BAsO_3OH]_8[AsO_4]_2[CsCl_4]Cl)_2$) ($0.06 \times 0.06 \times 0.04$ mm^3) was also selected for X-ray diffraction on a Bruker Nonius KappaCCD system at 120(2) K. Crystallisation was in the tetragonal space group I4/m (no. 87) with a = 8.9660(13)Å and c = 25.244(5)Å, V = 2029.37(58)$Å^3$, Z = 2, ρ_{calcd} = 3.371gcm^{-3}. A total of 7714 reflections were collected by ϕ and ω scans in the range $2.91^o < \theta < 27.48^o$ using $Mo_{K\alpha}$ radiation (λ = 0.71073Å), of which 1195 were unique. The structure was solved and refined by full-matrix least-squares on F^2 using the Patterson method with SHELX-97[17]. There were 81 parameters and the hydrogen atoms were fixed at a calculated distance and refined in a riding mode. SADABS[18] was used to perform the absorption correction parameter refinement on 6397 reflections reduced R(int) from 0.1035 to 0.0458. Ratio of minimum to maximum apparent transmission: 0.513893. The given T_{min} (0.5303) and T_{max} (0.6358) were generated using the SHELX SIZE command. Lorentzian polarisation was corrected using scalepack[19]. The highest remaining peak 3.33, 0.51Å from Cl3. Final R1 value 0.0451 and wR 0.1214 for 1059 independent reflections ($I > 2\sigma(I)$).

Further details of 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 numbers 415589 and 415590.