Support information

Synthesis and Structure of QD-6: A Novel Aluminoborate Constructed From Unprecedented
[B@Al$_6$O$_{24}$] and Polyborate Clusters

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Experimental Section

Synthesis: QD-6 was prepared under hydrothermal conditions from a mixture of Al(i-PrO)$_3$ or
AlCl$_3$·6H$_2$O, NH$_4$B$_5$O$_8$·4H$_2$O, cyclopentylamine (CPA), pyridine and H$_2$O in a molar ratio of 1:
2.5: 5.5: 48: 61. Typically, 0.204 g of Al(i-PrO)$_3$ or 0.241 g of AlCl$_3$·6H$_2$O and 0.680 g of
NH$_4$B$_5$O$_8$·4H$_2$O were dissolved in a mixed solution of 1.00 mL of H$_2$O and 5.00 mL of pyridine,
and then 0.35 mL of CPA was slowly added under constant stirring. The resulting mixture was
stirred at ambient temperature for 6h, then sealed in a 25-mL Teflon-lined autoclave and heated at
170°C for 13 days. The autoclave was cooled to room temperature, and colorless prismatic single
crystals were separated from the solution by filtration, washed with distilled water and dried in air
(46% yield based on Al). Strictly controlling the molar quantity of the organic amine (ca. 5.0-5.5
mmol) is crucial for the formation of QD-6; otherwise, a known polyborate
(NH$_4$)$_2$[B$_{10}$O$_{14}$OH]·H$_2$O$^+$ would be obtained when more or less amounts of CPA were used.
Additionally, attempts to synthesize QD-6 from other aluminum sources such as Al$_2$O$_3$, Al$_2$(SO$_4$)$_3$
and Al(NO$_3$)$_3$, or by using boric acid as a boron source, were unsuccessful.

The experimental and simulated powder X-ray diffraction patterns are in good accordance with
each other, indicating the phase purity of the sample (Fig. S4). IR (KBr pellet, cm$^{-1}$): 3454 cm$^{-1}$
(OH), 1514 cm$^{-1}$ (CPA), 1370 cm$^{-1}$ (BO$_3$), 1275 cm$^{-1}$ (AlO$_4$), 1063 cm$^{-1}$ (BO$_4$) (Fig. S5).

Crystal data for QD-6: C$_{30}$H$_{159}$N$_{12}$O$_{153}$B$_{65}$Al$_{12}$, M$\text{r} = 4163.10$, trigonal, R-3 (No. 148). a =
23.7421(2) Å, \( c = 24.7699(3) \) Å, \( V = 12091.9(2) \) Å\(^3\), \( Z = 3 \), \( \rho = 1.715 \) mg·cm\(^{-3}\), \( \lambda = 0.71073 \) Å, 
\( \mu(\text{MoK}\alpha) = 0.219 \) mm\(^{-1}\), \( F(000) = 6384 \). A total of 77316 reflections were collected in the range of \( 3.43^\circ \leq \theta \leq 28.28^\circ \), of which 6616 were unique \( (R_{int} = 0.0601) \) and 4606 with \( I \geq 2\sigma(I) \) were collected for the analysis. The structure was solved and refined by full-matrix least squares on \( F^2 \) values (SHELXL-97). Non-H atoms were refined anisotropically. The final \( R_1 \) values were 0.0577 \( (I \geq 2\sigma(I)) \). The final \( wR(F^2) \) values were 0.1692 \( (I \geq 2\sigma(I)) \). The final \( R_1 \) values were 0.0869 (all data). The final \( wR(F^2) \) values were 0.1825 (all data). The goodness of fit on \( F^2 \) was 1.085. CCDC 803658 for QD-6 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

![Figure S1. The [Al\(_7\)O\(_{21}\)] cluster in PKU-8.](image1)

![Figure S2. Comparison of the undecane borate FBBs observed in Mg\(_3\)[B\(_{11}\)O\(_{15}\)(OH)\(_9\)] (a) Sr\(_2\)B\(_{11}\)O\(_{16}\)(OH)\(_3\)(H\(_2\)O) (b) and Pb\(_6\)B\(_{11}\)O\(_{18}\)(OH)\(_9\) (c).](image2)
Figure S3. A projection of the structure of QD-6 along the c-axis. AlO$_6$, green octahedra, BO4 and BO3, purple.

Figure S4. The XRD patterns of QD-6.

Figure S5. The IR spectra of QD-6.
Figure S6. The TG curve of QD-6.