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Powder diffraction study of $Ba(NH_4)_4(PO_3)_6$

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Key indicators

Powder X-ray study
T = 295 K
Mean σ(P–O) = 0.016 Å
R factor = 0.066
wR factor = 0.089
Data-to-parameter ratio = 7.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of barium tetraammonium poly{hexakis[phosphate(V)]} was solved by direct methods from laboratory X-ray powder diffraction data collected at room temperature. The trigonal crystal structure is isostructural with $BaCs_4(PO_3)_6$. The Ba^{2+} cation and one of the N atoms lie on a threefold axis, whereas all remaining non-H atoms are in general positions. The Ba^{2+} cation is bonded to nine O atoms from three polyphosphate chains to form a distorted tricapped trigonal prism as coordination polyhedron. Links between the polyphosphate chains and the Ba^{2+} ions result in a three-dimensional network, with tunnels and cavities filled by ammonium cations.

Comment

The title compound, $Ba(NH_4)_4(PO_3)_6$, (I), was synthesized previously by thermal reaction in the BaO–NH_4PO_3 system (Selevich *et al.*, 2005). Here, we report the crystal structure of this compound determined from laboratory X-ray powder diffraction data.

The asymmetric unit of (I) contains one Ba, two P, two N, six O and six H atoms. The Ba^{2+} ion and one N atom lie on a threefold axis, whereas all remaining non-H atoms are in general positions.

The polyphosphate chains (Fig. 1), with a period of four tetrahedra, run parallel to the *c* axis. The lengths of the terminal P—O bonds lie within the range 1.43 (4)–1.54 (3) Å, whereas those of the bridging P—O bonds are significantly longer, in the range 1.581 (17)–1.628 (19) Å. The averages of the P—O bond lengths are 1.545 Å in the P1 tetrahedron and 1.544 Å in the P2 tetrahedron, which are in very good agreement with the value of 1.545 Å reported by Durif (1995) for an

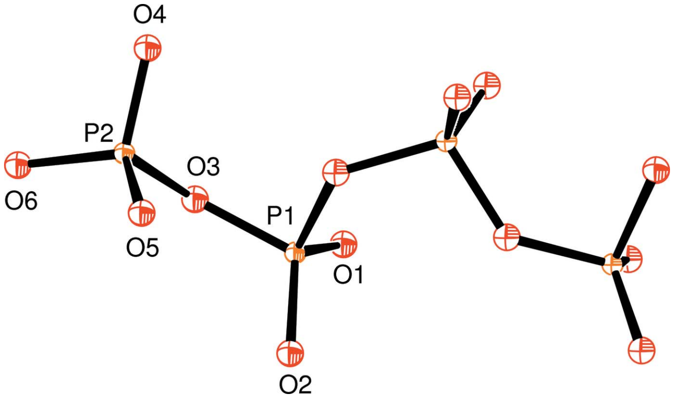

Figure 1
The repeat unit of the polyphosphate chain in the structure of (I), with the labelling of P and O atoms for the asymmetric unit. Displacement spheres are plotted at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator (y, x, $z + \frac{1}{2}$).

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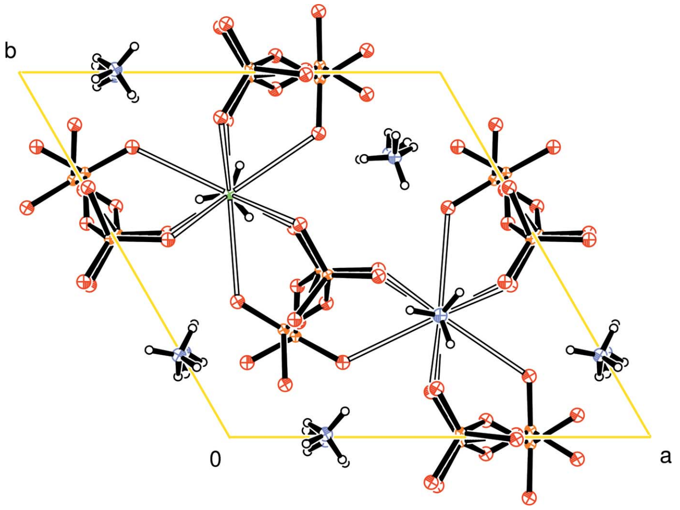

Figure 2
The crystal structure of (I), viewed along the *c* axis. Displacement spheres are drawn at the 50% probability level. Ba atoms are shown as green, N as blue, O as red and P as orange. H atoms are displayed as open spheres of arbitrary radii. Ba—O bonds are shown as hollow, and N—H and P—O bonds as solid.

average value of the P—O distances in any tetrahedron in condensed phosphates. Moreover, the O—P—O and P—O—P angles are characteristic for polyphosphate chains (Table 1).

The Ba^{2+} ion is coordinated by nine O atoms, forming a distorted tricapped trigonal prism. Each Ba^{2+} ion interlinks three polyphosphate chains, leading to a three-dimensional network with tunnels and cavities filled by ammonium cations (Fig. 2). The N1 atoms lie on threefold axes in the cavities. Considering N···O distances shorter than 3.2 Å, they are surrounded by six O atoms with N···O distances between 3.02 (5) and 3.155 (17) Å. The calculated positions of the H atoms of the $N1H_4$ cation lead to N—H···O angles between 124 and 172°. The N2 atoms, being on general sites, are located in tunnels extending along the *c* axis. Atom N2 is surrounded by seven O atoms, with N···O distances between 2.83 (7) and 3.20 (5) Å and N—H···O angles between 130 and 162°.

Compound (I) is isostructural with $BaCs_4(PO_3)_6$, which was investigated previously by Averbuch-Pouchot & Durif (1986). In comparison with (I), $BaCs_4(PO_3)_6$ shows larger unit-cell dimensions [a = 11.549 (5) and c = 9.114 (5) Å], which reflects the difference in the size of ammonium and caesium cations. The greater elongation of the lattice parameter *a* compared with the lattice parameter *c* is probably caused by the fact that the polyphosphate chains extend along the *c* axis, which restricts elongation of the unit cell in this direction.

Experimental

A mixture of BaO and NH_4PO_3 in the molar ratio 1:8 was placed in a wide silica crucible and kept under atmospheric conditions at 573 K in a laboratory furnance. Progress of the reaction was monitored by periodic sampling using both X-ray diffraction and optical microscopy. The resulting colourless microcrystalline material of (I) was washed with water on a glass filter and dried at room temperature.

Crystal data

$Ba(NH_4)_4(PO_3)_6$
$M_r = 683.32$
Trigonal, *P*31*c*
$a = 11.1936$ (2) Å
$c = 8.9393$ (3) Å
$V = 970.00$ (4) Å^3
$Z = 2$
$D_x = 2.340$ Mg m^{-3}
Cu *Kα* radiation
$\lambda = 1.5418$ Å
$T = 295$ K
Specimen shape: flat sheet
30 × 30 × 1 mm
Specimen prepared at 573 K
Particle morphology: needle-like, colourless

Data collection

Carl Zeiss (Jena) HZG-4A diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
Scan method: step
$2\theta_{min} = 8$, $2\theta_{max} = 105°$
Increment in $2\theta = 0.02°$

Refinement

Refinement on I_{net}
$R_p = 0.066$
$R_{wp} = 0.089$
$R_{exp} = 0.156$
$R_B = 0.045$
$S = 0.6$
Excluded region(s): none
Profile function: pseudo-Voight; the refined value of the η parameter is 0.692(13).
388 reflections
49 parameters
H-atom parameters constrained
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max} = 0.001$
Preferred orientation correction: Marsh–Dollase function (Marsh, 1932; Dollase, 1986); correction for the [001] preferred orientation of needle-like grains; refined parameters $G_1 = 1.39(2)$, $G_2 = 0.09(4)$.

Table 1
Selected geometric parameters (Å, °).

Ba—O1^{i}	2.73 (5)	P1—O6^{ii}	1.628 (19)
Ba—O2	2.91 (2)	P2—O3	1.581 (14)
Ba—O5	2.877 (17)	P2—O4	1.50 (2)
P1—O1	1.43 (4)	P2—O5	1.488 (19)
P1—O2	1.54 (3)	P2—O6	1.604 (14)
P1—O3	1.581 (17)		
O1—P1—O2	118 (2)	O3—P2—O5	102.7 (12)
O1—P1—O3	109 (2)	O3—P2—O6	106.0 (9)
O1—P1—O6^{ii}	110.2 (19)	O4—P2—O5	116.8 (12)
O2—P1—O3	114.1 (18)	O4—P2—O6	109.0 (18)
O2—P1—O6^{ii}	111.6 (16)	O5—P2—O6	113.8 (16)
O3—P1—O6^{ii}	91.2 (9)	P1—O3—P2	134.5 (11)
O3—P2—O4	107.6 (14)	P1^{i}—O6—P2	127.0 (12)

Symmetry codes: (i) $y, x, z - \frac{1}{2}$; (ii) $y, x, z + \frac{1}{2}$.

The powder diffraction pattern could be indexed with the program *TREOR90* (Werner *et al.*, 1985) in the hexagonal/trigonal system (F_{20} = 342, M_{20} = 225, F_{32} = 373, M_{32} = 198), with lattice parameters (see *Crystal Data*) close to those for $BaCs_4(PO_3)_6$ (Averbuch-Pouchot & Durif, 1986). Because the space group *P*31*c* for the caesium salt did not contradict the diffraction data for the ammonium compound, it was supposed that the two compounds are isostructural, although no close resemblance was found in their diffraction patterns. This was confirmed further by finding a reasonable structure solution for (I) in space group *P*31*c* using direct methods with *EXPO* (Altomare *et al.*, 1999). All non-H atoms were located, with R_F = 0.140. The solved structure was refined using the Rietveld method, as implemented in the program *FULLPROF* (Rodrigues-Carvajal, 2001). For reflections up to 40° 2θ, a correction for profile asymmetry was performed. A Marsh–Dollase correction (Marsh, 1932; Dollase, 1986) of intensities for a preferred orientation in the [001] direction of the needle-like grains was applied. The refined values of the preferred orientation

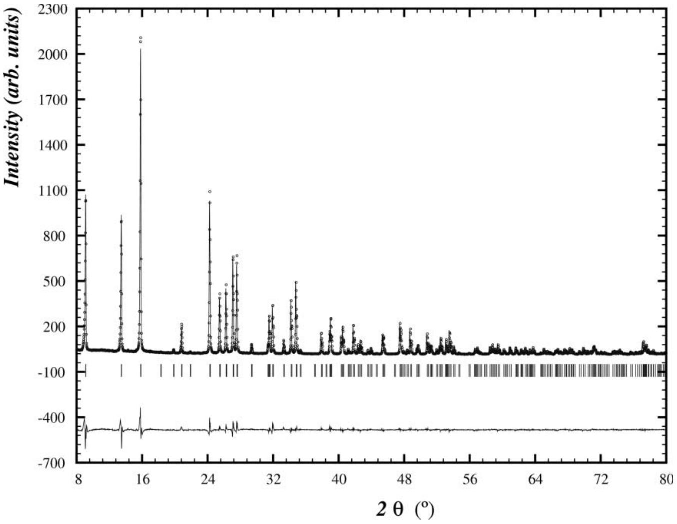

Figure 3
Final plots of the Rietveld refinement, showing the experimental (circles) and calculated (line) intensities of (I) in the range 8–80° 2θ. The difference plot appears below. Vertical markers refer to the calculated positions of the Bragg reflections of (I).

coefficients were $G_1 = 1.39\,(2)$ and $G_2 = 0.09\,(4)$. The atomic displacement parameters of all atoms were refined isotropically, those for N and O atoms being refined as one parameter. Furthermore, the structure was refined with soft restraints on P—O bond lengths, based on a geometric analysis of a large number of condensed phosphates. The H atoms of the two ammonium cations were placed in calculated positions, with N—H distances of 0.85 Å and H—N—H angles typical for a tetrahedron and assuming that all H atoms participate in hydrogen bonding with reasonable N···O distances and N—H···O angles. The placement of H atoms allowed slight improvements of $R_{\rm p}$ from 0.074 to 0.066, $R_{\rm wp}$ from 0.100 to 0.089, and $R_{\rm Bragg}$ from 0.069 to 0.045. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 3.

Data collection: local program; cell refinement: *FULLPROF* (Rodrigues-Carvajal, 2001); data reduction: local program; program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1999); program(s) used to refine structure: *FULLPROF*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *FULLPROF* and *PLATON* (Spek, 2003).

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