Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

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The crystal structure of the beta phase of ammonium pentaborate tetrahydrate, $\beta - NH_4B_5O_6(OH)_4 \cdot 2H_2O$

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **47** (1969), n.1-2, p. 85–99.

Accademia Nazionale dei Lincei

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Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1969.

Cristallografia. — *The crystal structure of the beta phase of ammonium pentaborate tetrahydrate,* β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$. Nota (*) di STEFANO MERLINO (**), presentata dal Socio E. ONORATO.

RIASSUNTO. — Il composto β–$NH_4B_5O_8 \cdot 4H_2O$ è monoclino con quattro molecole nella cella elementare; il gruppo spaziale è $C2/c$ e le costanti reticolari sono: $a = 11.65$, $b = 8.66$, $c = 11.40$ Å, $\beta = 93°\ 10'$. La struttura è stata risolta mediante sintesi di Patterson e di Fourier, utilizzando circa 800 riflessi indipendenti registrati con la camera di Weissenberg. Il raffinamento è stato effettuato con il metodo dei minimi quadrati. Il fattore di discordanza finale è risultato $R = 0.071$.

La struttura contiene gli ioni complessi $[B_5O_6(OH)_4]^-$ trovati per la prima volta da Zachariasen nella struttura del pentaborato di potassio tetraidrato; la formula strutturale del composto è quindi $NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$.

Lo ione ammonio è coordinato da otto atomi di ossigeno. Le molecole d'acqua e i gruppi ossidrilici formano legami idrogenici.

INTRODUCTION.

P. Toledano and M. A. Hebrard Matringe [1] ascertained the existence, in the ternary system of ammonium borates in presence of water, of a new pentaborate tetrahydrate, β–$NH_4B_5O_8 \cdot 4\,H_2O$.

The α phase of $NH_4B_5O_8 \cdot 4\,H_2O$ is isostructural with $KB_5O_8 \cdot 4\,H_2O$, whose crystal structure was determined by Zachariasen [2] and refined by Zachariasen and Plettinger [3].

The structure of β–$NH_4B_5O_8 \cdot 4\,H_2O$ was investigated, as a contribution to a research program in the field of hydrated borates developed in our laboratory, with the object of establishing a comparison with the structure of $KB_5O_8 \cdot 4\,H_2O$ and fixing its position in the crystal-chemical classification of borates.

EXPERIMENTAL.

The crystals were kindly supplied by P. Toledano; they were colourless. On the basis of two-circle goniometer measurements the crystals were assigned to the monoclinic system, prismatic class; this was subsequently confirmed by structural data. The forms exhibited are, according to the below reported orientation of axes: $c = \{001\}$, $o = \{111\}$, $p = \{11\bar{1}\}$. Most of the crystals are elongated along $[1\bar{1}0]$ (Fig. 1); some of them are tabular $\{001\}$. There is a distinct cleavage parallel to $\{100\}$.

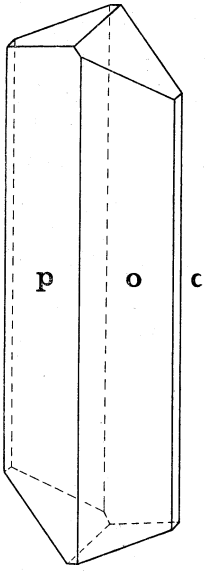

Fig. 1. – Drawing of a crystal of β–$NH_4B_5O_8 \cdot 4\,H_2O$.

(*) Pervenuta all'Accademia il 21 luglio 1969.

(**) Istituto di Mineralogia e Petrografia dell'Università di Pisa.

The crystal data were determined by means of rotation photographs, obtained with the CuKα radiation, and precession photographs taken with MoKα radiation.

β–Ammonium pentaborate tetrahydrate β–$NH_4B_5O_8 \cdot 4\,H_2O$, *M.W.* 272.15.

Monoclinic, space group $C2/c$ or Cc, from systematic absences: *hkl*, absent for $h + k = 2n + 1$, *h*0*l* absent for $l = 2n + 1$.

$$a = 11.65 \pm 0.02 \text{ Å}$$
$$b = 8.66 \pm 0.01 \text{ Å}$$
$$c = 11.40 \pm 0.02 \text{ Å}$$
$$\beta = 93^0\ 10' \pm 10'$$

Unit cell volume $V = 1148.5$ Å^3, $Z = 4$

$D_m = 1.59\ \text{g} \cdot \text{cm}^{-3}$ (determined with a Westphal type balance)

$D_x = 1.57\ \text{g} \cdot \text{cm}^{-3}$, F(000) = 560

$\mu = 14.2\ \text{cm}^{-1}$ (CuKα).

The intensity data were recorded with nickel-filtered CuKα radiation ($\lambda = 1.5418$ Å), by means of Weissenberg photographs, with the multiple film technique and integration process. A fragment elongated in the *b* direction was cut from a large crystal; it was reduced to cylindrical shape with a radius of 0.027 cm. ($\mu R = 0.383$ for CuKα radiation). Eight layers with *b* as rotation axis ($k = 0$ through 7) were taken. A total of 1097 independent reflexions (819 observed) was collected. The intensities, measured with a Nonius microdensitometer, have been corrected for Lorentz and polarization factors, for the incipient but incomplete $\alpha_1 - \alpha_2$ spot doubling and for the absorption factor using the three-constants formula proposed by Palm [4] for cylindrical crystals. A secondary extinction correction was applied in the final stages of the refinement.

TABLE I.

Statistical averages and distributions of $|E|$.

	Experimental	Centrosymmetric	Noncentrosymmetric
$\langle \|E\| \rangle$	0.737	0.798	0.886
$\langle \|E^2 - 1\| \rangle$ . . .	1.022	0.968	0.736
$\langle \|E^2\| \rangle$	1.000	1.000	1.000
$\|E\| > 3$	0.2%	0.3%	0.01%
$\|E\| > 2$	5.5%	5.0%	1.8%
$\|E\| > 1$	30.5%	32.0%	36.8%

By means of the DATFIX program, incorporated in the Crystal Structures Calculations System X-Ray 63 [5], an overall isotropic temperature factor, the scale factors for the intensity data and the normalized structure factor magnitudes E were calculated. The method of calculation of the estimated parameters is based upon the normal statistics of the E magnitudes. The statistical averages and distribution of E are given in Table I, compared with the theoretical values for both a centro-symmetric and a noncentro-symmetric distribution of atoms in the unit cell. The unobserved reflexions were given zero intensity. The experimental values in Table I correspond to a crystal with a center of symmetry; the choice of the space group $C2/c$ was subsequently confirmed by structure analysis.

DETERMINATION AND REFINEMENT OF THE STRUCTURE.

It was assumed as a good working hypothesis (and an indication in this sense was offered by the value of the density very close to the value 1.567 $g \cdot cm^{-3}$ found for the phase α [6]) that even the structure of β-$NH_4B_5O_8 \cdot 4\,H_2O$ should be characterized by insular polyons $[B_5O_6(OH)_4]^-$. Because the general position in the space group $C2/c$ has eightfold multiplicity, such a polyon must be in fourfold special position. Now the polyon would have ideally point symmetry $\bar{4}2\,m$ (D_2d): four of the five fourfold positions in the space group, 4 (a-d), are at centers of symmetry and are thus immediately ruled out. The remaining special position 4 (e) is on the twofold axis. Of the three twofold axes of $[B_5O_6(OH)_4]^-$ one is parallel to the elongation direction of the polyon; thus, taking into account the cell parameters dimensions, the twofold axis of the space group must coincide, as in the structure of $KB_5O_8 \cdot 4\,H_2O$, with one of the two remaining binary axes of the polyon.

The ammonium ion also must be placed on the twofold axis or, admitting spherical symmetry around the nitrogen atom, on a symmetry center. The water molecule can be placed in general position.

The orientation of the pentaborate ion around the symmetry axis was found from the Patterson projection along [010]. Structure factors were calculated with the coordinates found for the atoms of the anion from the Patterson projection. With the signs thus obtained, the electron density projected along [010] was calculated. This showed that the structure proposed for anion was correct, that the ammonium ion is placed on the twofold axis and gave the x and z coordinates for the water molecule.

On the basis of packing considerations, y coordinates were proposed for the atoms of the pentaborate group. Three cycles of full-matrix least-squares refinement of the resulting set of three-dimensional positional parameters were computed, by means of the ORFLS program [7] adapted to the X-Ray 63 System. Only the $h0l$, $h1l$ and $h2l$ reflexions were introduced in the first two cycles, whereas in the third cycle the full range of intensity data was used. The scale factors and an overall isotropic temperature factor

were included among the refined parameters; their starting values were those obtained by the DATFIX program.

The R_1 value for the observed reflexions resulted 0.36 ($R_1 = \Sigma \big| |F_o| - |F_c| \big| / \Sigma |F_o|$).

A three-dimensional Fourier synthesis was then computed with the use of the signs based on the contributions of the polyon atoms. The electron density map showed both the nitrogen atom along the twofold axis and the oxygen atom of the water molecule in general position as well resolved peaks. A structure factor calculation, made at this point, gave a reliability index $R_1 = 0.25$. By a careful survey of the calculated structure factors few mistakes in estimating intensities and indexing reflexions were corrected.

Three least-squares refinement cycles with individual isotropic temperature factors reduced the reliability index to $R_1 = 0.147$. A difference map showed regions of strong positive and negative electron density at right angles to each other, which is characteristic of considerable anisotropic motion.

Refinement was therefore continued with anisotropic temperature factors in the form:

$$\exp \{-(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2\, hk\, \beta_{12} + 2\, hl\, \beta_{13} + 2\, kl\, \beta_{23})\}.$$

The restrictions to the thermal ellipsoids of the nitrogen and boron atoms lying on the twofold axis are that $\beta_{12} = \beta_{23} = 0$ [8]. Three more least-squares cycles were carried out: because of the degeneracy between β_{22} and the scale factors, these were rescaled after each cycle but not refined in the least-squares process.

A comparison of the values of F_o and F_c showed some secondary extinction effect. A correction was applied according to the formula

$$I_{corr.} = I_{obs.} [1 - g\, I_{obs.}]^{-1}$$

where the coefficient g was adjusted to give the best fit.

At this stage the reliability index was $R_1 = 0.083$. A three-dimensional difference Fourier synthesis showed smearing of the electron density around the nitrogen atom and four well resolved peaks in positions where the hydrogen atoms of the hydroxyl groups and the water molecule were expected on the basis of stereochemical considerations. Then a scattering curve for a spherically symmetrical ammonium ion was substituted to the scattering curve for nitrogen; the hydrogen atoms were included in the structure factor calculations with isotropic temperature factors $B = 5.0$ Å^2. The reliability index decreased to $R_1 = 0.078$ and, after two least-squares cycles, in which the parameters of hydrogen atoms were not refined, to $R_1 = 0.071$, whereas $R_2 = [\Sigma w \big| |F_o| - |F_c| \big|^2 / \Sigma w\, |F_o|^2]^{1/2}$ was 0.089. Unit weights were assigned initially, but at the beginning of the anisotropic refinement the following weighting scheme, based on the plot of ΔF *vs* F_o, was introduced:

$w = 0$ for unobserved reflexions

$\sqrt{w} = 1$ for observed reflexions with $F_o \leq 7$

$\sqrt{w} = 1/(0.07\, F_o + 0.5)$ for observed reflexions with $F_o > 7$

TABLE II.

Observed and calculated structure factors.

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FO	FC
2	0	0	91.7	107.9	1	1	3	35.1	34.3	2	2	1	60.5	-76.5	-10	2	11	19.1	-21.6
6	0	0	31.0	-28.0	3	1	3	22.7	-20.6	4	2	1	53.0	-59.1	-8	2	11	12.5	-13.3
8	0	0	50.4	-56.7	5	1	3	23.2	-18.9	6	2	1	22.2	-20.0	-6	2	11	6.1	-7.9
10	0	0	31.4	29.4	7	1	3	52.7	-57.9	8	2	1	47.3	51.5	-4	2	11	9.5	9.4
12	0	0	10.9	-9.7	9	1	3	12.4	-10.3	10	2	1	11.7	11.3	-2	2	11	12.7	12.4
-14	0	2	44.0	-49.6	13	1	3	9.8	-9.8	12	2	1	7.0	7.9	0	2	11	11.3	9.6
-12	0	2	43.9	-46.2	-11	1	4	6.8	-6.8	-14	2	2	11.6	11.5	2	2	11	16.6	-16.0
-10	0	2	16.5	-16.2	-9	1	4	19.8	-18.5	-12	2	2	26.1	28.0	4	2	11	28.1	-30.7
-8	0	2	30.5	28.1	-7	1	4	38.9	-39.3	-10	2	2	35.3	36.7	8	2	11	6.1	-6.1
-6	0	2	66.7	66.0	-5	1	4	67.1	72.5	-6	2	2	5.3	-4.1	-4	2	12	11.9	-12.6
-4	0	2	50.9	-52.0	-3	1	4	20.2	15.3	-4	2	2	48.3	-46.7	-2	2	12	30.5	-33.9
-2	0	2	16.7	-14.2	-1	1	4	5.6	-4.5	-2	2	2	55.7	-59.9	0	2	12	17.2	-18.3
0	0	2	55.2	43.6	3	1	4	75.5	-86.8	0	2	2	32.7	30.5	4	2	12	15.9	-16.0
2	0	2	22.0	18.9	5	1	4	45.5	45.9	2	2	12	15.6	-16.3	-6	2	13	13.6	13.9
4	0	2	47.5	-48.5	7	1	4	10.3	-8.2	2	2	2	14.0	-12.1	-4	2	13	14.0	-13.2
6	0	2	32.1	-31.1	9	1	4	11.8	-11.4	4	2	2	5.3	6.7	0	2	13	20.1	21.5
8	0	2	15.5	-14.2	11	1	4	20.7	21.1	6	2	2	26.2	26.1	4	2	13	16.0	16.7
10	0	2	10.2	-10.3	13	1	4	5.1	-4.3	10	2	2	20.7	19.6	-2	2	14	9.1	-11.2
12	0	2	8.5	-8.0	-11	1	5	8.3	7.3	12	2	2	13.0	13.1	0	2	14	6.9	6.7
14	0	2	21.2	-21.8	-7	1	5	47.8	48.8	-14	2	3	12.9	-12.1	1	3	0	25.4	29.6
-12	0	4	25.2	-25.1	-5	1	5	33.7	30.1	-12	2	3	12.2	11.4	3	3	0	19.0	20.3
-10	0	4	18.6	17.6	-1	1	5	15.6	-11.6	-10	2	3	45.6	49.5	5	3	0	9.9	9.0
-8	0	4	19.1	17.0	1	1	5	58.3	-59.0	-8	2	3	18.8	17.0	7	3	0	5.9	5.0
-6	0	4	54.9	52.5	3	1	5	18.5	16.5	-6	2	3	36.8	-36.2	9	3	0	35.2	-37.0
-4	0	4	59.3	59.4	5	1	5	23.5	-21.3	-4	2	3	68.9	-75.6	11	3	0	21.6	-21.0
-2	0	4	42.5	-37.8	7	1	5	18.9	-16.8	-2	2	3	62.7	-65.6	-11	3	1	9.5	-6.9
0	0	4	155.5	195.1	11	1	5	14.3	-13.9	0	2	3	41.2	36.2	-9	3	1	46.2	-48.3
2	0	4	37.5	37.0	13	1	5	9.4	-10.1	2	2	3	58.6	-62.2	-7	3	1	7.1	7.6
4	0	4	9.5	9.3	-11	1	6	19.7	20.0	4	2	3	25.3	20.7	-5	3	1	48.2	-51.4
6	0	4	47.5	47.4	-7	1	6	7.6	-6.6	6	2	3	17.6	15.9	-3	3	1	28.0	-25.4
8	0	4	18.9	-17.4	-5	1	6	16.1	13.0	8	2	3	21.4	-21.1	-1	3	1	22.6	21.4
10	0	4	30.3	30.3	-3	1	6	16.5	-14.1	10	2	3	7.2	-7.8	1	3	1	22.8	-23.0
12	0	4	11.7	-9.3	-1	1	6	10.6	10.0	12	2	3	29.0	-31.4	3	3	1	52.1	60.6
14	0	4	16.2	-16.7	1	1	6	9.9	-8.7	-8	2	4	23.8	-21.5	5	3	1	28.0	-28.2
-12	0	6	16.5	-17.1	3	1	6	25.7	21.0	-6	2	4	14.8	-13.7	7	3	1	10.0	-8.3
-10	0	6	14.0	-13.5	5	1	6	35.6	36.8	-4	2	4	34.6	-34.6	9	3	1	28.6	28.4
-8	0	6	21.7	-20.6	9	1	6	16.5	-16.3	-2	2	4	64.7	-68.7	11	3	1	14.6	14.0
-6	0	6	20.5	16.1	13	1	6	6.7	5.9	0	2	4	7.5	-6.7	-13	3	2	9.4	-9.3
-4	0	6	48.1	-47.2	-5	1	7	14.5	13.9	2	2	4	67.9	-69.7	-11	3	2	13.2	-13.5
-2	0	6	13.7	10.2	-3	1	7	15.2	13.9	4	2	4	53.8	-55.2	-9	3	2	24.3	-22.9
0	0	6	87.0	91.4	-1	1	7	33.1	29.2	6	2	4	9.1	-7.8	-7	3	2	19.2	-17.6
2	0	6	58.1	58.1	1	1	7	58.3	60.1	8	2	4	15.5	-14.2	-5	3	2	48.0	51.0
4	0	6	16.6	-13.1	3	1	7	7.8	5.1	10	2	4	19.3	18.2	-3	3	2	13.0	13.5
6	0	6	65.2	-73.9	5	1	7	32.8	-31.7	12	2	4	9.5	10.4	-1	3	2	22.1	16.5
8	0	6	46.7	-52.0	7	1	7	59.9	-71.4	-14	2	5	8.3	-7.8	1	3	2	34.7	-32.2
10	0	6	15.9	-16.4	9	1	7	36.3	-38.9	-12	2	5	10.3	10.4	3	3	2	108.8	-130.4
12	0	6	9.8	9.8	11	1	7	5.5	4.7	-8	2	5	6.8	4.6	5	3	2	30.4	-30.0
-12	0	8	21.0	-23.4	-7	1	8	24.5	-24.5	-6	2	5	28.7	25.3	7	3	2	5.5	-5.9
-8	0	8	35.4	36.9	-5	1	8	25.2	23.9	-4	2	5	16.6	-14.6	9	3	2	9.6	8.7
-6	0	8	65.3	69.8	-1	1	8	29.6	-26.3	-2	2	5	100.2	118.6	11	3	2	14.1	12.8
-4	0	8	68.6	74.4	1	1	8	14.0	11.2	0	2	5	19.0	16.7	13	3	2	5.9	-5.4
-2	0	8	44.4	-42.1	3	1	8	20.6	-20.3	2	2	5	54.1	-51.0	-7	3	3	9.7	6.8
0	0	8	20.8	17.0	5	1	8	47.2	51.2	4	2	5	25.9	-24.1	-3	3	3	76.1	-85.7
2	0	8	9.0	7.6	7	1	8	15.8	15.3	6	2	5	29.0	-28.6	-1	3	3	25.7	-21.3
6	0	8	50.7	54.2	9	1	8	32.2	-34.1	8	2	5	39.0	42.0	1	3	3	34.5	33.0
10	0	8	20.1	20.5	11	1	8	8.9	-8.8	10	2	5	14.7	14.5	3	3	3	58.5	56.9
-8	0	10	26.2	-26.3	-7	1	9	45.1	48.0	-12	2	6	10.1	10.9	5	3	3	62.5	67.5
-6	0	10	9.9	8.0	-5	1	9	51.5	55.9	-10	2	6	24.8	25.5	7	3	3	19.7	-19.3
-4	0	10	12.7	-12.9	-3	1	9	12.3	10.4	-8	2	6	6.5	5.8	9	3	3	20.0	19.9
-2	0	10	19.8	-18.3	-1	1	9	8.2	-8.1	-6	2	6	13.2	11.5	11	3	3	14.0	13.5
0	0	10	14.3	13.0	1	1	9	45.4	-47.9	-4	2	6	22.1	-19.0	-11	3	4	20.8	20.8
2	0	10	10.0	-10.2	5	1	9	15.2	-14.1	-2	2	6	48.1	-47.9	-9	3	4	12.0	11.2
-4	0	12	17.5	17.6	7	1	9	33.4	-34.7	2	2	6	20.5	-18.2	-7	3	4	23.0	22.0
0	0	12	42.3	46.4	9	1	9	7.2	-8.5	6	2	6	29.2	29.2	-5	3	4	20.8	-17.6
2	0	12	45.9	51.4	-11	1	10	5.2	5.4	8	2	6	14.3	13.2	-3	3	4	50.5	-50.3
6	0	12	14.1	13.1	-9	1	10	18.2	-19.4	10	2	6	19.1	18.7	-1	3	4	11.7	-8.8
-4	0	14	6.5	5.3	-7	1	10	22.5	-21.8	12	2	6	9.0	9.2	1	3	4	12.8	11.8
-2	0	14	19.5	-19.9	-5	1	10	27.4	27.4	-10	2	7	22.7	23.0	3	3	4	24.0	22.1
2	0	14	16.8	-16.2	-3	1	10	29.7	28.9	-8	2	7	20.9	19.5	5	3	4	11.2	9.5
1	1	0	9.6	9.1	-1	1	10	35.5	38.2	-6	2	7	26.4	-24.2	7	3	4	11.5	12.2
3	1	0	66.9	-78.8	1	1	10	12.3	-11.6	-4	2	7	38.1	-36.2	9	3	4	9.6	-10.9
5	1	0	53.6	57.3	3	1	10	29.9	-31.6	-2	2	7	30.2	-29.3	11	3	4	14.5	-14.6
7	1	0	37.1	-35.9	-9	1	11	7.8	7.4	0	2	7	30.8	26.9	-13	3	5	7.0	-5.5
11	1	0	26.5	25.8	-7	1	11	16.9	18.1	2	2	7	28.8	-26.4	-11	3	5	8.9	-9.1
-13	1	1	28.5	29.5	-5	1	11	29.0	30.3	4	2	7	36.4	-36.5	-9	3	5	40.6	-44.5
-11	1	1	23.1	21.6	-3	1	11	16.9	16.3	6	2	7	6.9	-6.7	-7	3	5	11.8	12.4
-9	1	1	20.7	-20.4	-1	1	11	25.5	-25.6	8	2	7	8.0	-7.6	-5	3	5	10.6	-7.5
-7	1	1	6.2	-5.6	1	1	11	25.5	-27.1	10	2	7	22.0	22.2	-3	3	5	35.3	-31.7
-5	1	1	46.1	-50.4	3	1	11	17.3	-18.3	-8	2	8	17.7	-16.3	1	3	5	51.1	-51.3
-3	1	1	24.4	22.3	7	1	11	5.9	-5.3	-6	2	8	26.2	-25.8	3	3	5	44.5	43.5
-1	1	1	75.9	84.2	-9	1	12	10.1	9.5	-4	2	8	36.8	-38.0	9	3	5	27.6	28.2
1	1	1	44.2	44.4	-7	1	12	12.7	-13.9	-2	2	8	45.7	-47.5	11	3	5	6.7	6.2
3	1	1	41.3	42.1	1	1	12	12.2	11.5	0	2	8	6.0	5.1	-11	3	6	7.0	-6.8
5	1	1	70.0	-68.9	5	1	12	8.8	8.5	2	2	8	8.2	-6.4	-9	3	6	12.6	-11.5
7	1	1	45.4	-49.5	7	1	12	13.7	13.6	4	2	8	20.5	-18.0	-7	3	6	21.5	-19.9
9	1	1	15.5	-15.8	-5	1	13	11.4	11.5	8	2	8	22.5	-22.5	-5	3	6	21.6	19.8
11	1	1	13.2	-11.9	-1	1	13	11.4	11.5	-10	2	9	14.9	15.9	1	3	6	11.3	11.4
-11	1	2	20.5	20.7	1	1	13	11.9	-11.3	-8	2	9	17.0	16.5	3	3	6	61.1	-66.5
-7	1	2	14.0	11.9	-1	1	14	13.8	15.0	-6	2	9	25.4	23.0	5	3	6	28.6	-25.0
-5	1	2	16.7	12.9	3	1	14	17.7	-16.5	-4	2	9	49.9	-52.6	7	3	6	8.8	-8.1
-3	1	2	37.9	-37.5	2	2	0	102.1	-136.6	-2	2	9	13.7	-12.3	11	3	6	11.7	10.8
-1	1	2	35.5	-33.1	4	2	0	45.3	-51.5	0	2	9	8.1	9.5	-9	3	7	11.1	-11.1
3	1	12	18.8	-19.3	6	2	0	16.7	13.6	2	2	9	13.4	12.2	-7	3	7	7.9	-7.4
3	1	2	65.4	73.3	10	2	0	22.9	22.1	4	2	9	52.1	58.1	-3	3	7	28.2	-26.1
5	1	2	60.8	66.6	12	2	0	5.8	5.0	6	2	9	7.3	6.8	-1	3	7	10.9	-6.3
7	1	2	11.6	7.7	14	2	0	6.5	-5.2	8	2	9	7.4	8.1	1	3	7	30.8	28.6
9	1	2	27.6	-29.7	-14	2	1	12.8	-12.0	10	2	9	14.7	-13.7	3	3	7	31.1	30.6
-13	1	3	9.7	-10.1	-12	2	1	31.7	34.0	-10	2	10	5.2	5.6	5	3	7	36.7	38.0
-9	1	3	12.2	11.1	-10	2	1	15.9	14.9	-6	2	10	13.0	11.8	7	3	7	12.0	-12.0
-7	1	3	29.8	28.8	-8	2	1	13.3	12.6	-4	2	10	10.5	7.6	9	3	7	8.6	8.7
-5	1	3	63.0	67.9	-6	2	1	3.4	3.8	-2	2	10	10.7	-9.6	11	3	7	23.6	22.7
-3	1	3	10.6	8.2	-4	2	1	6.2	3.8	0	2	10	16.1	14.4	-11	3	8	12.7	13.6
-1	1	3	25.9	24.4	0	2	1	11.5	-9.8	4	2	10	13.8	-12.0	-9	3	8	5.8	6.4

Continued: TABLE II.

H	K	L	FO	FC	H	K	L	FC	FC	H	K	L	FC	FC	H	K	L	FO	FC
-7	3	8	16.2	16.7	12	4	6	15.1	-13.4	-5	5	5	9.8	10.6	2	6	7	43.8	-43.9
-5	3	8	8.7	9.4	-12	4	7	9.1	8.1	-3	5	6	6.9	-5.8	4	6	7	17.7	16.9
-3	3	8	13.2	-12.2	-10	4	7	7.5	-8.4	-1	5	6	16.8	-15.7	8	6	7	7.8	8.1
-1	3	8	11.8	10.7	-8	4	7	19.7	-20.0	1	5	6	25.3	22.6	-6	6	8	21.8	23.8
1	3	8	14.2	-12.3	-6	4	7	7.0	-8.8	5	5	6	14.8	13.7	-4	6	8	13.8	14.6
3	3	8	35.8	-34.4	-2	4	7	47.1	49.8	7	5	6	23.6	23.5	0	6	8	40.9	-41.4
5	3	8	34.3	-35.0	0	4	7	51.4	53.4	9	5	6	12.0	12.1	2	6	8	37.6	-37.7
9	3	8	30.6	30.7	2	4	7	11.5	10.7	-9	5	7	10.6	-9.7	8	6	8	21.1	21.1
11	3	8	26.6	26.2	4	4	7	20.6	19.0	-7	5	7	29.1	30.1	-8	6	9	6.4	-6.4
-9	3	9	22.5	-24.1	10	4	7	5.9	6.3	-5	5	7	14.2	13.5	-6	6	9	11.1	-10.6
-7	3	9	6.0	5.8	-10	4	8	6.8	6.9	-3	5	7	9.2	-8.8	-4	6	9	11.4	11.6
-3	3	9	44.7	-46.9	-8	4	8	22.6	-22.8	-1	5	7	11.0	-9.1	-2	6	9	17.4	17.6
-1	3	9	17.1	-14.5	-6	4	8	16.3	-14.9	1	5	7	61.1	-73.2	0	6	9	19.2	19.0
1	3	9	28.2	-28.0	-4	4	8	14.9	-13.0	3	5	7	30.0	-29.5	4	6	9	9.3	-9.1
3	3	9	42.6	45.1	-2	4	8	52.7	56.9	5	5	7	7.2	6.1	-6	6	10	15.2	-14.8
5	3	9	38.5	40.4	0	4	8	45.5	47.2	9	5	7	8.5	8.7	-4	6	10	17.4	-15.9
7	3	9	11.3	-11.1	2	4	8	16.2	15.2	-9	5	8	11.4	-12.8	-2	6	10	11.1	-11.1
-9	3	10	19.9	20.6	6	4	8	17.1	-16.5	-5	5	8	18.3	-18.4	0	6	10	29.5	-30.9
-7	3	10	6.0	5.6	10	4	8	8.0	-7.6	-3	5	8	12.1	-11.6	2	6	10	11.9	-12.3
-5	3	10	15.0	-14.3	-10	4	9	7.2	-7.5	-1	5	8	42.5	44.3	6	6	10	16.9	16.4
-3	3	10	47.1	-53.1	-8	4	9	13.6	-14.1	1	5	8	37.5	38.1	-4	6	11	24.9	-24.3
-1	3	10	46.4	-50.1	-2	4	9	19.2	19.2	3	5	8	36.3	37.9	2	6	11	10.0	-9.7
1	3	10	14.1	13.8	2	4	9	42.6	-45.2	5	5	8	18.9	-18.3	4	6	11	11.4	10.6
3	3	10	8.4	7.4	4	4	9	21.1	-20.8	7	5	8	19.1	-17.4	-2	6	12	7.7	7.9
5	3	10	11.8	12.8	6	4	9	21.0	-21.3	-1	5	9	33.1	34.0	1	7	0	3.4	2.8
9	3	10	8.8	-9.1	8	4	9	7.7	6.7	1	5	9	14.7	14.3	3	7	0	20.1	-22.1
-9	3	11	21.9	-23.6	-8	4	10	14.6	13.3	3	5	9	10.7	-10.2	5	7	0	46.3	-49.1
-7	3	11	9.0	-8.5	-4	4	10	7.7	6.9	5	5	9	9.3	8.0	7	7	0	20.8	-21.5
-5	3	11	11.3	10.1	0	4	10	13.7	13.6	9	5	9	7.9	7.4	9	7	0	8.5	9.6
-3	3	11	10.1	10.6	2	4	10	22.7	22.7	-7	5	10	14.8	14.5	-9	7	1	6.8	-7.5
-1	3	11	9.5	9.9	6	4	10	10.9	11.7	1	5	10	30.1	30.9	-7	7	1	32.9	-34.6
1	3	11	27.0	28.6	8	4	10	22.4	-22.7	3	5	10	12.9	11.7	-5	7	1	36.9	-37.7
7	3	11	10.2	9.5	-8	4	11	15.1	15.6	5	5	10	10.8	-11.2	-3	7	1	36.8	-38.0
-5	3	12	9.1	9.8	-6	4	11	13.6	11.9	7	5	10	10.2	-8.3	-1	7	1	6.4	4.5
-3	3	12	9.0	-8.6	-4	4	11	12.3	-12.3	-7	5	11	9.7	8.9	1	7	1	4.3	4.2
-3	3	12	18.8	-17.9	0	4	11	10.2	9.4	-5	5	11	7.2	-6.8	3	7	1	10.1	8.5
-1	3	13	4.9	5.5	4	4	11	13.1	13.4	-3	5	11	16.8	-17.6	5	7	1	44.1	47.2
1	3	13	10.3	-11.5	6	4	11	11.2	11.3	-1	5	11	18.5	19.7	7	7	1	5.4	-5.6
3	3	13	12.7	12.1	-6	4	12	19.4	17.5	3	5	11	9.6	-8.4	9	7	1	10.1	-9.7
-1	3	14	22.7	-23.4	-4	4	12	9.6	9.6	5	5	11	13.5	-14.0	-9	7	2	12.7	15.7
2	4	0	20.8	20.4	-2	4	12	16.8	17.2	-5	5	12	22.4	22.7	-7	7	2	22.1	21.5
4	4	0	41.2	45.6	0	4	12	9.6	9.2	-1	5	12	4.4	4.8	-5	7	2	29.3	-28.8
6	4	0	42.2	46.9	4	4	12	11.2	11.5	2	6	0	25.5	27.1	-3	7	2	10.2	-10.0
10	4	0	29.3	-29.4	-4	4	13	19.3	-19.7	6	6	0	15.2	-11.8	-1	7	2	16.7	-16.1
-12	4	1	12.9	12.3	0	4	13	12.8	13.2	10	6	0	15.1	-14.9	3	7	2	34.2	34.7
-10	4	1	26.0	-25.9	2	4	13	11.4	-10.5	12	6	0	12.0	11.6	5	7	2	16.3	-14.5
-8	4	1	42.5	-47.1	1	5	0	25.1	-29.3	-12	6	1	8.3	-8.6	-9	7	3	24.8	-25.8
-6	4	1	38.4	-40.7	3	5	0	7.3	7.1	-8	6	1	28.5	29.2	-5	7	3	7.4	-8.6
-4	4	1	66.8	-74.9	5	5	0	5.7	-4.0	-6	6	1	59.3	68.5	-3	7	3	35.3	34.4
-2	4	1	24.0	21.8	7	5	0	53.8	61.2	-4	6	1	21.0	20.6	-1	7	3	47.9	49.0
0	4	1	9.6	10.2	9	5	0	18.6	17.9	-2	6	1	31.7	-34.8	1	7	3	13.4	-13.2
4	4	1	40.8	44.4	13	5	0	12.6	-11.1	0	6	1	8.8	-9.4	7	7	3	19.0	18.5
6	4	1	13.4	-13.4	-13	5	1	17.8	-15.7	2	6	1	21.2	-22.5	9	7	3	17.8	18.5
8	4	1	8.2	-8.5	-9	5	1	27.2	27.4	4	6	1	36.5	38.2	-9	7	4	6.8	-6.1
18	4	1	12.0	-11.9	-7	5	1	64.2	75.8	8	6	1	17.1	-17.3	-5	7	4	13.1	-12.6
12	4	1	18.0	-18.3	-5	5	1	53.8	61.4	10	6	1	13.3	14.2	-3	7	4	9.0	-8.0
-10	4	2	13.1	-11.7	-3	5	1	7.2	-6.5	12	6	1	15.9	-13.6	-1	7	4	19.5	-17.3
-8	4	2	52.3	-60.5	1	5	1	45.9	-46.3	-10	6	2	15.0	-14.3	1	7	4	18.2	-18.2
-6	4	2	21.7	-21.7	5	5	1	28.9	31.1	-8	6	2	13.1	12.4	3	7	4	14.9	-15.4
-4	4	2	57.2	63.8	7	5	1	26.5	-25.8	-6	6	2	22.0	21.7	5	7	4	26.7	-26.7
-2	4	2	34.4	34.3	13	5	1	12.5	9.9	-4	6	2	24.1	23.6	7	7	4	13.8	-14.6
0	4	2	59.9	60.1	-13	5	2	7.8	6.8	0	6	2	42.3	-42.2	-9	7	5	5.3	5.3
2	4	12	10.4	-10.9	-9	5	2	8.3	8.4	2	6	2	29.2	-29.8	-7	7	5	16.4	-16.6
2	4	2	24.3	-20.4	-7	5	2	16.3	-14.6	4	6	2	22.8	-21.8	-7	7	5	16.4	-16.6
4	4	2	10.6	10.8	-5	5	2	15.7	-12.9	6	6	2	10.1	-10.9	-5	7	5	30.9	-32.1
6	4	2	23.6	22.7	-3	5	2	12.8	-12.7	12	6	2	17.7	15.7	-3	7	5	29.2	-29.7
8	4	2	25.1	-25.1	-1	5	2	36.6	36.7	-12	6	3	16.8	16.7	-1	7	5	6.5	-6.1
12	4	2	8.2	-7.7	1	5	2	62.1	60.5	-10	6	3	22.8	-23.9	1	7	5	10.5	8.7
-10	4	3	20.5	-19.7	3	5	12	9.3	10.1	-6	6	3	30.6	30.6	5	7	5	29.5	31.7
-8	4	3	23.1	-21.8	9	5	2	10.4	10.4	-2	6	3	28.0	26.2	9	7	5	9.5	-9.0
-6	4	3	11.9	11.0	-13	5	3	9.5	8.1	0	6	3	39.1	-35.7	-9	7	6	8.2	8.5
-4	4	3	15.4	13.3	-9	5	3	11.4	-13.6	2	6	3	24.7	-22.7	-7	7	6	18.7	18.2
-2	4	3	65.2	68.9	-7	5	3	24.6	24.1	6	6	3	34.1	-36.4	-5	7	6	21.4	-21.3
0	4	3	40.2	38.0	-5	5	3	12.8	-11.1	-12	6	4	18.1	18.9	-3	7	6	8.9	-8.9
2	4	3	30.9	-28.3	-3	5	3	7.6	-7.2	-8	6	4	10.9	10.1	-1	7	6	8.2	-6.6
4	4	3	27.0	23.2	-1	5	3	10.2	9.3	-6	6	4	12.2	11.3	3	7	6	28.4	27.5
6	4	3	7.3	7.5	1	5	3	57.7	-58.8	-4	6	4	9.9	-11.1	5	7	6	10.9	-10.5
8	4	3	21.7	21.6	3	5	3	10.1	-9.1	-2	6	4	8.8	-8.8	7	7	6	7.1	-7.4
10	4	3	23.7	25.1	5	5	3	10.4	-9.9	0	6	4	45.2	-39.3	9	7	6	4.3	3.4
-12	4	4	16.0	15.5	7	5	3	26.5	-26.0	4	6	4	15.2	14.7	-9	7	7	12.9	-11.6
-8	4	4	15.2	-13.8	9	5	3	10.0	-10.8	6	6	4	9.6	9.9	-7	7	7	6.1	5.6
-2	4	4	54.9	56.4	11	5	3	17.5	-16.9	8	6	4	9.3	9.5	-5	7	7	8.1	-9.2
2	4	4	35.8	32.8	-7	5	4	22.5	21.8	10	6	4	15.2	-15.7	-1	7	7	41.9	41.5
4	4	4	36.0	35.1	-5	5	4	25.0	-24.4	-10	6	5	10.2	10.1	3	7	7	17.8	16.7
10	4	4	29.2	-30.5	-1	5	4	34.0	32.9	-6	6	5	13.0	14.5	5	7	7	12.3	10.6
-10	4	5	8.6	-8.4	1	5	4	24.5	22.9	-4	6	5	12.4	11.7	-3	7	8	10.2	-10.2
-8	4	5	18.9	-19.1	3	5	4	34.7	33.9	-2	6	5	10.8	-10.2	-1	7	8	31.7	-32.4
-4	4	5	46.2	-46.9	5	5	4	27.2	-25.6	0	6	5	17.9	15.9	1	7	8	27.0	-27.4
0	4	5	16.6	-13.2	7	5	4	10.9	12.1	4	6	5	18.3	17.0	5	7	8	5.6	5.9
2	4	5	32.2	-30.6	9	5	4	8.7	8.5	8	6	5	27.7	-28.8	-7	7	9	6.3	-5.1
4	4	5	31.2	29.4	-11	5	5	9.2	9.5	10	6	5	10.8	11.4	-5	7	9	5.4	-5.3
8	4	5	9.8	8.7	-9	5	5	9.2	8.2	-10	6	6	8.4	-8.6	-3	7	9	13.0	12.6
12	4	5	22.6	-22.5	-7	5	5	23.8	23.8	-4	6	6	7.5	8.7	-1	7	9	10.4	9.9
-12	4	6	7.1	-6.8	-5	5	5	25.3	24.4	0	6	6	22.1	-20.1	3	7	9	35.1	-37.8
-8	4	6	14.8	-15.3	-3	5	5	8.2	6.0	2	6	6	12.1	-9.6	5	7	9	21.0	-18.3
-6	4	6	6.6	-7.3	-1	5	5	34.3	35.4	4	6	6	16.8	-15.9	-5	7	10	4.6	-4.2
-4	4	6	48.1	50.4	5	5	5	11.8	11.2	6	6	6	12.3	-13.0	-3	7	10	15.0	14.4
-2	4	6	12.5	10.2	7	5	5	27.3	-30.2	8	6	6	8.4	-9.8	-1	7	10	11.5	11.4
0	4	6	7.4	7.1	9	5	5	11.8	-11.7	10	6	6	6.3	-5.7	1	7	10	16.3	-16.0
2	4	6	30.6	-27.1	-11	5	6	11.5	-12.9	-10	6	7	10.4	-10.1	-3	7	11	23.7	-23.6
4	4	6	9.7	-7.9	-9	5	6	10.6	11.0	-6	6	7	33.0	33.9	-1	7	11	10.6	9.3

$\bar{2}21$ reflexion was escluded from the refinement, being too strong on the last film. The shifts of all the parameters in the last cycle were well within their standard deviations, with an average $\Delta/\sigma = 0.12$, defining Δ as the change in a parameter in the last least-squares cycle and σ as the e.s.d. of the parameter in that cycle.

The scattering factors used in the structure factor calculations were taken from International Tables for X–Ray Crystallography [9] for boron, oxygen and hydrogen atoms, and from Davis and Whitaker [10] for the ammonium ion with spherical symmetry.

The observed and calculated factors are compared in Table II. Tables III, IV and V give the final positional and thermal parameters with their standard deviations.

TABLE III.

Final atomic coordinates and their standard deviations (in parentheses).

	x	*y*	*z*
O(1)	0.6153(2)	0.1003(4)	—0.0209(2)
O(2)	0.4648(2)	0.2690(3)	—0.0023(2)
O(3)	0.3121(2)	0.4446(3)	0.0080(2)
O(4)	0.5655(2)	0.1751(3)	0.1721(2)
O(5)	0.4173(2)	0.3731(3)	0.1816(2)
O(6)	0.2969(2)	0.6176(3)	0.2759(2)
B(1)	0.5000	0.2758(6)	0.2500
B(2)	0.5503(3)	0.1806(5)	0.0531(3)
B(3)	0.3980(3)	0.3616(4)	0.0646(3)
N	0.5000	0.8288(5)	0.2500

TABLE IV.

Final anisotropic thermal parameters ($\times 10^4$) *and their standard deviations (in parentheses).*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	51(2)	129(5)	22(2)	72(2)	—3(1)	—14(2)
O(2)	37(2)	62(4)	12(1)	40(2)	—4(1)	—6(2)
O(3)	45(2)	73(5)	25(2)	49(2)	—6(1)	—2(2)
O(4)	30(1)	28(3)	14(1)	20(2)	—4(1)	1(2)
O(5)	40(2)	23(4)	16(1)	24(2)	—1(1)	—5(2)
O(6)	47(2)	58(4)	28(2)	19(2)	9(1)	18(2)
B(1)	29(3)	5(8)	12(3)	0	—2(2)	0
B(2)	26(2)	42(6)	21(2)	22(3)	1(2)	—2(3)
B(3)	28(2)	13(6)	19(2)	10(2)	0(2)	—1(2)
N	60(3)	49(8)	18(3)	0	4(2)	0

TABLE V.

Hydrogen atom parameters used in the calculation of the final structure factors.

	x	y	z	B(Å^2)
H(1)	0.334	0.530	0.243	5.0
H(2)	0.236	0.654	0.246	5.0
H(3)	0.307	0.400	—0.063	5.0
H(4)	0.686	0.054	0.018	5.0

DESCRIPTION AND DISCUSSION OF THE STRUCTURE.

The principal structural features of β–$NH_4B_5O_8 \cdot 4\,H_2O$ are illustrated in Fig. 2 and 3. The crystal contains the characteristic double ring polyion of composition $[B_5O_6(OH)_4]^-$ consisting of one boron-oxygen tetrahedron and four boron-oxygen triangles linked at corners. This same polyion was firstly found by Zachariasen [2] in $KB_5O_6(OH)_4 \cdot 2\,H_2O$ and is also present in its ammonium relative α–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$. Thus the structural

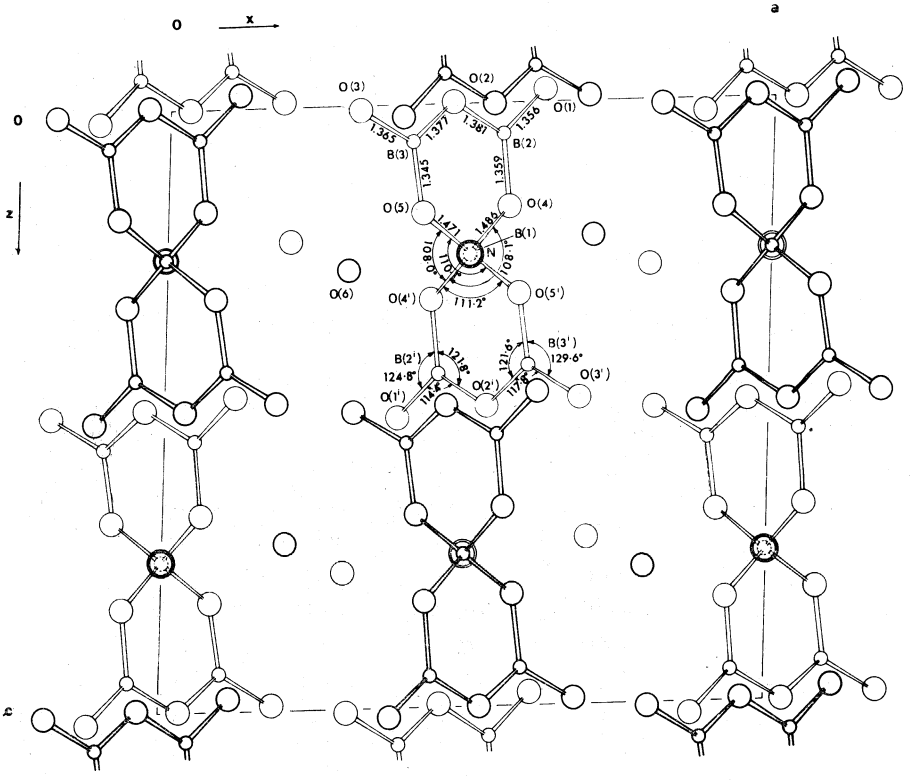

Fig. 2. – The crystal structure of β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$ viewed along [010].

formula of the beta phase of ammonium pentaborate tetrahydrate is: β–$NH_4\,B_5O_6(OH)_4 \cdot 2\,H_2O$. The infinite chains found in larderellite, $NH_4B_5O_7(OH)_2 \cdot H_2O$ [11], consist of the polymerization product of these insular polyions, according to the schematic reaction:

$$n\,[B_5O_6(OH)_4]^- = [B_5O_7(OH)_2]_n^{-n} + nH_2O\,.$$

The insular polyions in β–$NH_4\,B_5O_6(OH)_4 \cdot 2\,H_2O$ are linked through ammonium-oxygen bonds and through hydrogen bonds *via* the water molecules

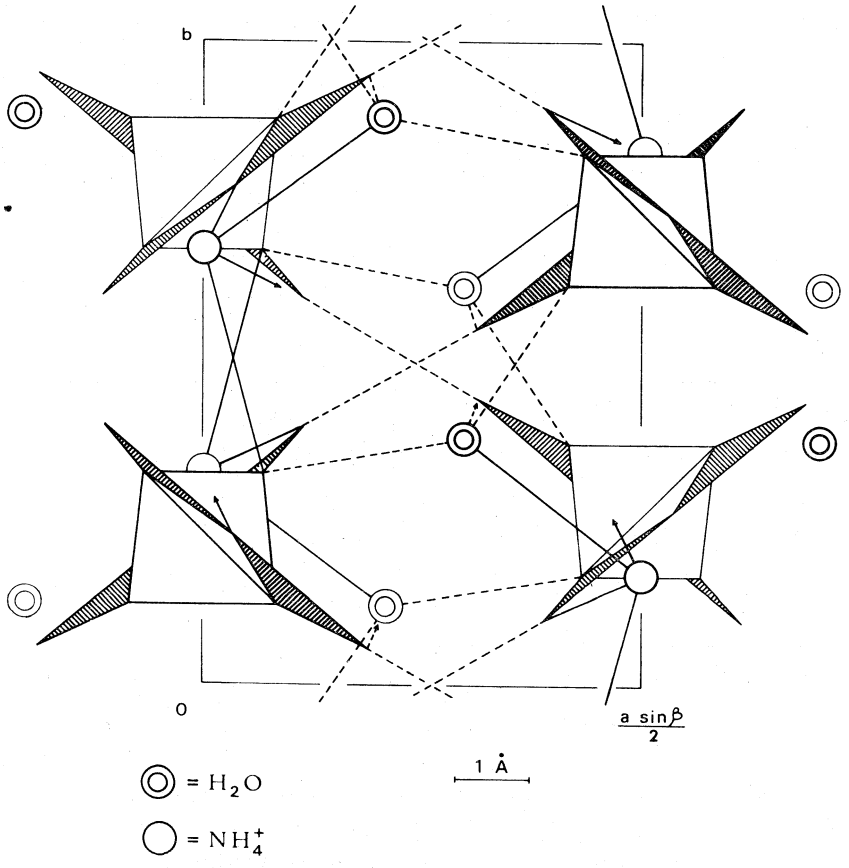

Fig. 3. – The crystal structure of β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$ viewed along [001]. The dashed lines represent hydrogen bonds. The continuous lines represent NH_4—O bonds. Dashed and continuous lines ending with an arrow indicate that the bond is associated with an oxygen atom translated one unit in the [001] direction.

to form zig-zag strings along [001]; adjacent strings are linked only through additional hydrogen bonds. These structural features are represented in Fig. 3, where the structure is described in terms of boron coordination triangles and tetrahedra. The distinct cleavage parallel to {100} is easily understood from the preceding discussion and from consideration of Fig. 3.

TABLE VI.

Boron-oxygen bond lengths and bond angles in β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$.

TRIANGULARLY COORDINATED BORON:

Atoms	Distances	e.s.d.	Atoms	Angles	e.s.d.
B(2)—O(1) . . .	1.356 Å	0.005 Å	O(1)—B(2)—O(2)	114°24′	17′
O(2) . . .	1.381	0.005	O(1)—B(2)—O(4)	123°46′	19′
O(4) . . .	1.359	0.004	O(2)—B(2)—O(4)	121°49′	19′
B(3)—O(2) . . .	1.377	0.005	O(2)—B(3)—O(3)	117°50′	17′
O(3) . . .	1.365	0.005	O(2)—B(3)—O(5)	121°37′	17′
O(5) . . .	1.345	0.004	O(3)—B(3)—O(5)	120°34′	18′
Average	1.364 Å			120°0′	

TETRAHEDRALLY COORDINATED BORON:

Atoms	Distances	e.s.d.	Atoms	Angles	e.s.d.
B(1)—O(4) . . .	1.486 Å	0.004 Å	O(4)—B(1)—O(4^i)	108°8′	26′
O(4^i) . .	1.486		O(5)—B(1)—O(5^i)	110°7′	26′
O(5) . .	1.471	0.004	O(4)—B(1)—O(5)	111°13′	19′
O(5^i) . .	1.471		O(4^i)—B(1)—O(5^i)	111°13′	
			O(4)—B(1)—O(5^i)	108°2′	19′
			O(5)—B(1)—O(4^i)	108°2′	
Average	1.479 Å			109°27′	

Boron-oxygen bond lengths and bond angles are reported in Table VI. and in Fig. 2. In this and in the following Tables as well as in Fig. 2, the atoms of the different asymmetric units are related to the atoms of the fundamental unit as follows:

i	atom at	$1-x$	y	$1/2-z$
ii	atom at	x	$1-y$	$1/2+z$
iii	atom at	$1-x$	$1-y$	$-z$
iv	atom at	x	$1+y$	z
v	atom at	$1-x$	$1+y$	$1/2-z$
vi	atom at	$1/2+x$	$-1/2+y$	z
vii	atom at	x	$1-y$	$-1/2+z$
viii	atom at	$-1/2+x$	$1/2+y$	z

The average B—O distance in the triangles is 1.364 Å and in the tetrahedron 1.479 Å, in excellent agreement with the results previously found in other borates by various workers.

TABLE VII.

Average boron-oxygen bond lengths and, in parentheses, their standard deviations, in $KB_5O_6(OH)_4 \cdot 2\,H_2O$ *and* β–$NH_4B_0O_6(OH)_4 \cdot 2\,H_2O$.

Compound	Triangle		Tetrahedron
	B—O*	B—O**	
$KB_5O_6(OH)_4 \cdot 2\,H_2O$	1.352(3) Å	1.372(4) Å	1.478(4) Å
β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$	1.356(3)	1.379(4)	1.479(3)

In Table VII the average boron-oxygen bond lengths in β–$NH_4B_5O_6(OH)_4 \cdot 2\,H_2O$ are compared with the corresponding values found in $KB_5O_6(OH)_4 \cdot 2\,H_2O$; in this Table O* and O** represent respectively oxygen atoms linked to only one boron in trigonal state and oxygen atoms linked to two boron atoms in trigonal state. The average bond lengths for B—O* and B—O** are appreciably different in both compounds. Coulson [12, 13] and Coulson and Dingle [14] explain the differences of bond lengths of trigonal B—O bonds with differences in π–bond order. The π–bond orders should clearly be smaller for a B—O** bond than for B—O* bond; Coulson and Dingle, using simple Huckel theory, obtained π–bond orders of 0.447 and 0.512 for B—O** and B—O* respectively.

Coulson and Dingle in their treatment correlate the differences in bond length with molecular structure. On the other hand Zachariasen [15] has used Pauling's valence neutralization concept to explain the variations in B—O bond lengths on the basis of the crystal structure. The situation is very similar to that found in the field of silicates structures where the variations in the Si—O distances can be explained in terms of *d*—*p* π—bonding theory suggested by Cruickshank [16], or on the basis of the Pauling-Zachariasen method of the balancing of valences. However, as in the case of Si—O bonds, also for trigonal B—O bonds the two theories are not exclusive and, following the same reasoning as Pant [17], it can be said that " π–bonding in trigonal B—O bonds may be part of the mechanism whereby valency balance is achieved ".

The presence of a π–electrons system is confirmed by the planarity of the B_2O_5 groups formed by the coordination triangles the least-squares plane in Table VIII was calculated following Schomaker, Waser, Marsh and Bergmann [18], with all weights equal to 1.

TABLE VIII.

Least-squares plane.

EQUATION IN THE FORM $Ax+By+Cz=D$ WHERE x, y AND z ARE FRACTIONAL COORDINATES

A	B	C	D	Atoms defining the plane
7.5989	6.5349	—1.2066	5.3058	O(1), O(2), O(3), O(4), O(5), B(1), B(2), B(3)

DEVIATIONS FROM PLANE (Å)

O(1)	O(2)	O(3)	O(4)	O(5)	B(1)	B(2)	B(3)
—0.050	0.014	0.038	0.072	—0.084	0.006	0.008	—0.004

The NH_4—O distances are listed in Table IX: there are four oxygen atoms, two hydroxyls and two water molecules at distances between 2.936 Å and 3.230 Å, with an average distance of 3.046 Å.

TABLE IX.

Ammonium-oxygen bond lengths. The estimated standard deviations are 0.005 Å.

NH_4—$O(1^{ii})$	2.936 Å
NH_4—$O(1^{iii})$	2.936
NH_4—$O(2^{ii})$	2.998
NH_4—$O(2^{iii})$	2.998
NH_4—$O(4^{iv})$	3.230
NH_4—$O(4^{v})$	3.230
NH_4—O(6)	3.018
NH_4—$O(6^{i})$	3.018

TABLE X.

Distances shorter than 3.0 Å *between oxygen atoms not bonded to the same boron atom* (e.s.d. 0.005 Å).

$O(1)\cdots O(3^{vi})$	2.665 Å
$O(3)\cdots O(6^{vii})$	2.696
$O(6)\cdots O(5)$	2.788
$O(6)\cdots O(4^{viii})$	2.927

The hydrogen atoms of the hydroxyl groups and of the water molecule were located, as it was said in the preceding section, by means of a Fourier difference synthesis. The resulting system of hydrogen bonds can also be

deduced unequivocally from Table X, which lists the distances shorter than 3.0 Å between oxygen atoms not bonded to the same boron atom: the oxygen atoms O(4) and O(5) are proton acceptors from the water molecule; O(1) and O(3) are proton donors to O(3) and O(6) respectively. An independent confirmation of this distribution of hydrogen bonds is given by the valence balance which is shown in Table XI. A strength of 1/8 was assigned to each NH_4—O bond; the strengths of the O—H and H···O bonds were assumed to be 0.8 and 0.2 respectively.

TABLE XI.

Valence balance in β–$NH_4B_5O_6(OH)_4 \cdot 2\ H_2O$.

	B(1)	B(2)	B(3)	NH_4	H(1)	H(2)	H(3)	H(4)	Σ
O(1)		1.00		0.125*				0.80	1.93
O(2)		1.00	1.00	0.125*					2.13
O(3)			1.00				0.80	0.20	2.00
O(4)	0.75*	1.00		0.125*		0.20			2.08
O(5)	0.75*		1.00		0.20				1.95
O(6)				0.125*	0.80	0.80	0.20		1.93
Σ	3.00	3.00	3.00	1.00	1.00	1.00	1.00	1.00	

* Two bonds for cation, one for anion.

THERMAL MOTION.

Table XII gives for each atom the root mean square displacements along the principal axes of the thermal ellipsoids and the angles which they make with the axes of a cartesian system. The latter is defined as follows: axis 1 is in the direction of vector $\overrightarrow{O(2)\,B(1)}$; axis 2 is in the direction of [axis 1]× $\times[\overrightarrow{O(2)\,O(3)}]$; axis 3 is in the direction of [axis 1]×[axis 2].

As we have previously said the atoms B(2), B(3) and O(1), O(2), O(3), O(4) and O(5) form nearly coplanar groups B_2O_5. It is seen, from the data reported in Table VIII, that the maximum thermal displacement for these atoms is in the direction of axis 2, which is parallel to the normal of the B_2O_5 group. The O(1) and O(3) atoms, which form only one O—B bond each, show the largest thermal motion and the greatest anisotropy.

TABLE XII.

Analysis of anisotropic thermal parameters.

ϑ_1, ϑ_2 and ϑ_3 are the angles of the principal axes of the thermal ellipsoids with respect to axes 1, 2 and 3 of the cartesian system defined in the text.

Atom	Principal axis	R.M.S. displacement	ϑ_1	ϑ_2	ϑ_3
O(1)	1	0.059	101°	90°	11°
	2	0.119	168	88	101
	3	0.284	92	178	90
O(2)	1	0.061	94	84	7
	2	0.085	176	89	94
	3	0.215	91	173	84
O(3)	1	0.059	75	83	16
	2	0.127	165	87	76
	3	0.235	91	173	83
O(4)	1	0.057	110	106	157
	2	0.099	159	81	71
	3	0.167	93	162	72
O(5)	1	0 047	81	112	155
	2	0.104	171	93	99
	3	0.184	91	157	67
O(6)	1	0.104	42	114	123
	2	0.139	127	92	143
	3	0.209	108	156	75
B(1)	1	0.045	89	140	130
	2	0.086	178	90	92
	3	0.143	92	130	40
B(2)	1	0 075	92	82	8
	2	0.118	178	91	92
	3	0.168	89	172	82
B(3)	1	0.055	88	122	148
	2	0.112	178	91	92
	3	0.145	90	148	58
N	1	0.109	9	84	96
	2	0.136	91	40	50
	3	0.204	81	130	42

This work was supported by Consiglio Nazionale delle Ricerche, Roma.

All the calculations were performed on the IBM 7090 computer of Centro Nazionale Universitario di Calcolo Elettronico (C.N.U.C.E.) Pisa.

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