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Refinement of the Structure of Hilgardite-1A

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Abstract

The fundamental building block of the title compound, dicalcium nonaoxopentaborate chloride hydrate, $Ca_2[B_5O_9]Cl.H_2O$, is the $[B_5O_{12}]^{9-}$ polyanion; translationally equivalent polyanions link to form chains parallel to the *c* axis. These chains are cross-linked, forming a zeolite-type borate framework. There are two Ca sites; Ca(1) has hexagonal bipyramidal coordination and Ca(2) has pentagonal bipyramidal coordination.

Comment

Hilgardite-1A is one of three known polymorphs of $Ca_2[B_5O_9]Cl.H_2O$; the others are hilgardite-3A (Wan & Ghose, 1983) and hilgardite-4M (Ghose & Wan, 1979). The relationships between the polymorphs have been considered by Ghose (1982). These borate minerals are of considerable interest as they are thought to be possible precursors of a new family of borate zeolites (Ghose & Wan, 1979; Wan & Ghose, 1983). This observation is supported by the recent discovery of zeolite-type borate frameworks in the minerals pringleite and ruitenbergite (Grice, Burns & Hawthorne, 1994).

As part of recent studies of the occurrence of borate minerals in the Sussex, New Brunswick area (Burns, Stirling & Hawthorne, 1992; Grice, Burns & Hawthorne, 1994; Roberts *et al.*, 1993), we noted that both hilgardite-4M and hilgardite-1A occur there. The discovery at this locality of the rare hilgardite-1A provided the opportunity and the impetus to better characterize its structure, which was first reported by Rumonova, Iorysh & Belov (1977).

The structure of hilgardite-1A was determined and refined by Rumonova, Iorysh & Belov (1977) using intensity data collected with an automated diffractometer. Their refinement gave an *R* index of 0.074, which we considered suspiciously high; this work verifies their structure but with a final *R* index of 0.019. The atomic coordinates and bond lengths of the current work are significantly more precise than those given by Rumonova, Iorysh & Belov (1977), and we note that our refinement gives boron polyhedra that are significantly less distorted.

The structure of hilgardite-1A has been illustrated and described by Rumonova, Iorysh & Belov (1977). The fundamental building block of the structure is the anhydrous double-ring pentaborate polyanion $[B_5O_{12}]^{9-}$ (Fig. 1), which also occurs in hilgardite-4M, hilgardite-3A and garrelsite. In hilgardite-1A, each pentaborate polyanion is linked to a translationally equivalent polyanion along **c**, giving a repeat distance of 6.286 (1) Å. The borate chains link to identical chains through corner-sharing along the *a* and *b* axes, forming a zeolite-like borate framework. There are two Ca sites; Ca(1) occurs with hexagonal bipyramidal coordination and Ca(2) with pentagonal bipyramidal coordination. Adjacent Ca polyhedra share an edge to form a dimer; sharing of Cl^- between adjacent dimers forms chains parallel to [110].

Strontium hilgardite-1A has been reported by Braitsch (1959) and Hodenberg & Kühn (1977) [see Ghose (1985) for name clarification], and Rachlin *et al.* (1986) reported that some of the hilgardite-4M found in the Sussex, New Brunswick area contains significant strontium. The site scattering multipliers at the Ca(1) and Ca(2) site were included in the least-squares refinement, the values converging to 0.997 (4) and 1.008 (3) for the Ca(1) and Ca(2) sites, respectively, indicating that there is negligible Sr at these sites.

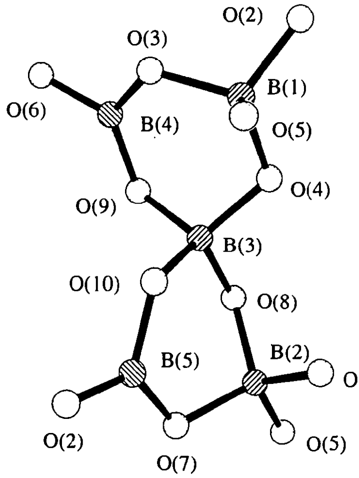

Fig. 1. The $[B_5O_{12}]^9$ pentaborate polyanion. B atoms are represented by parallel-hatched circles and O atoms by dot-filled circles.

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Experimental

The sample of hilgardite-1A was obtained from the Penobsquis potash deposit, Sussex, New Brunswick.

Crystal data

$Ca_2[B_5O_9]Cl.H_2O$
$M_r = 331.67$
Triclinic
$P1$
$a = 6.452$ (1) Å
$b = 6.559$ (1) Å
$c = 6.286$ (1) Å
$\alpha = 61.60$ (1)°
$\beta = 118.72$ (1)°
$\gamma = 105.86$ (1)°
$V = 204.90$ (6) Å^3
$Z = 1$

$D_x = 2.688$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 10$–26°
$\mu = 1.73$ mm^{-1}
$T = 297$ K
Irregular
0.24 × 0.16 × 0.08 mm
Colourless

Data collection

Nicolet $R3m$ diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical spherical
$T_{\min} = 0.820$, $T_{\max} = 0.966$
1286 measured reflections
1286 independent reflections
1256 observed reflections [$I > 2.5\sigma(I)$]

$\theta_{\max} = 30°$
$h = -7 \rightarrow 8$
$k = -7 \rightarrow 7$
$l = 0 \rightarrow 8$
2 standard reflections monitored every 50 reflections
intensity variation: 3%

Refinement

Refinement on F
$R = 0.019$
$wR = 0.025$
$S = 0.92$
1256 reflections
170 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + 0.000551F^*F]$
$(\Delta/\sigma)_{\max} < 0.05$

$\Delta\rho_{\max} = 0.38$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: isotropic
Extinction coefficient: 0.004 (1)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ca(1)	0	0	0	0.0088 (2)
Ca(2)	0.4524 (1)	0.5484 (1)	0.1099 (1)	0.0099 (2)
B(1)	0.4741 (4)	0.8707 (4)	0.4713 (4)	0.0047 (9)
B(2)	0.3306 (4)	0.0909 (4)	0.6016 (4)	0.0050 (9)
B(3)	0.5515 (4)	0.0245 (4)	0.0713 (5)	0.0062 (9)
B(4)	0.8823 (4)	0.0030 (4)	0.4837 (5)	0.0074 (10)
B(5)	0.4476 (4)	0.4211 (4)	0.7138 (5)	0.0072 (10)
O*W*(1)	0.8862 (4)	0.5813 (4)	0.2218 (4)	0.0213 (9)
O(2)	0.4477 (3)	0.6424 (3)	0.6750 (3)	0.0091 (7)
O(3)	0.7221 (3)	0.9630 (3)	0.5849 (3)	0.0080 (7)
O(4)	0.4205 (3)	0.8525 (3)	0.2258 (3)	0.0062 (6)
O(5)	0.3081 (3)	0.0276 (3)	0.4028 (3)	0.0066 (7)
O(6)	0.1080 (3)	0.0518 (3)	0.6372 (3)	0.0096 (7)
O(7)	0.3946 (3)	0.3499 (3)	0.5194 (3)	0.0087 (7)
O(8)	0.5119 (3)	0.9652 (3)	0.8620 (3)	0.0062 (7)
O(9)	0.8105 (3)	0.0102 (3)	0.2380 (3)	0.0092 (7)
O(10)	0.4851 (3)	0.2634 (3)	0.9706 (3)	0.0079 (7)
Cl	0.9796 (1)	0.4730 (1)	0.8121 (1)	0.0155 (2)
H(1)	0.926 (7)	0.477 (5)	0.180 (8)	
H(2)	0.982 (6)	0.557 (7)	0.410 (3)	

Table 2. *Interatomic distances* (Å), *angles* (°) *and hydrogen-bonding geometry* (Å, °)

B(1)—O(2)	1.469 (3)	B(5)—O(2)	1.352 (4)
B(1)—O(3)	1.490 (3)	B(5)—O(7)	1.373 (4)
B(1)—O(4)	1.468 (4)	B(5)—O(10)	1.381 (3)
B(1)—O(5$^{\rm i}$)	1.459 (4)	⟨B(5)—O⟩	1.369
⟨B(1)—O⟩	1.471		
		Ca(1)—O(5)	2.408 (2)
B(2)—O(5)	1.429 (4)	Ca(1)—O*W*(1$^{\rm vi}$)	2.503 (2)
B(2)—O(6)	1.494 (4)	Ca(1)—O(3$^{\rm vii}$)	2.439 (2)
B(2)—O(7)	1.519 (3)	Ca(1)—O(4$^{\rm ii}$)	2.596 (2)
B(2)—O(8$^{\rm ii}$)	1.460 (2)	Ca(1)—O(6$^{\rm iv}$)	2.542 (3)
⟨B(2)—O⟩	1.475	Ca(1)—O(8$^{\rm vii}$)	2.809 (2)
		Ca(1)—O(9$^{\rm viii}$)	2.374 (3)
B(3)—O(9)	1.486 (3)	Ca(1)—Cl$^{\rm ix}$	2.761 (1)
B(3)—O(4$^{\rm ii}$)	1.468 (3)	⟨Ca(1)—O,Cl⟩	2.554
B(3)—O(8$^{\rm iii}$)	1.434 (4)		
B(3)—O(10$^{\rm iv}$)	1.484 (4)	Ca(2)—O*W*(1)	2.509 (3)
⟨B(3)—O⟩	1.468	Ca(2)—O(4)	2.511 (3)
		Ca(2)—O(7)	2.435 (2)
B(4)—O(9)	1.363 (4)	Ca(2)—O(2$^{\rm iv}$)	2.486 (2)
B(4)—O(3$^{\rm ii}$)	1.367 (4)	Ca(2)—O(8$^{\rm iv}$)	2.449 (2)
B(4)—O(6$^{\rm v}$)	1.357 (3)	Ca(2)—O(10$^{\rm iv}$)	2.501 (3)
⟨B(4)—O⟩	1.362	Ca(2)—Cl$^{\rm ix}$	2.761 (1)
		⟨Ca(2)—O,Cl⟩	2.522
O(2)—B(1)—O(3)	107.2 (1)	O(9)—B(3)—O(4$^{\rm ii}$)	110.2 (2)
O(2)—B(1)—O(4)	111.0 (2)	O(9)—B(3)—O(8$^{\rm iii}$)	104.9 (3)
O(2)—B(1)—O(5$^{\rm i}$)	110.3 (2)	O(9)—B(3)—O(10$^{\rm iv}$)	109.0 (2)
O(3)—B(1)—O(4)	111.4 (2)	O(4$^{\rm ii}$)—B(3)—O(8$^{\rm iii}$)	108.9 (2)
O(3)—B(1)—O(5$^{\rm i}$)	110.1 (2)	O(4$^{\rm ii}$)—B(3)—O(10$^{\rm iv}$)	111.1 (3)
O(4)—B(1)—O(5$^{\rm i}$)	106.9 (2)	O(8$^{\rm iii}$)—B(3)—O(10$^{\rm iv}$)	112.5 (2)
⟨O—B(1)—O⟩	109.5	⟨O—B(3)—O⟩	109.4
O(5)—B(2)—O(6)	114.2 (2)	O(9)—B(4)—O(3$^{\rm ii}$)	120.8 (2)
O(5)—B(2)—O(7)	108.8 (2)	O(9)—B(4)—O(6$^{\rm v}$)	124.4 (3)
O(5)—B(2)—O(8$^{\rm ii}$)	112.2 (2)	O(3$^{\rm ii}$)—B(4)—O(6$^{\rm v}$)	114.5 (3)
O(6)—B(2)—O(7)	105.5 (2)	⟨O—B(4)—O⟩	119.9
O(6)—B(2)—O(8$^{\rm ii}$)	106.7 (2)		
O(7)—B(2)—O(8$^{\rm ii}$)	109.0 (2)	O(2)—B(5)—O(7)	125.3 (2)
⟨O—B(2)—O⟩	109.4	O(2)—B(5)—O(10)	113.0 (3)
		O(7)—B(5)—O(10)	121.4 (2)
		⟨O—B(5)—O⟩	119.9

D—H···A	D—H	H···A	D···A	D—H···A
O*W*(1)—H(1)···Cl$^{\rm iv}$	0.97	2.51	3.313 (1)	140
O*W*(1)—H(2)···Cl	0.99	2.33	3.195 (1)	146
H(1)—O*W*(1)···H(2)	0.97	0.99	1.62	111

Symmetry codes: (i) $x, 1+y, z$; (ii) $x, y-1, z$; (iii) $x, y-1, z-1$; (iv) $x, y, z-1$; (v) $1+x, y, z$; (vi) $x-1, y-1, z$; (vii) $x-1, y-1, z-1$; (viii) $x-1, y, z$; (ix) $x-1, y, z-1$.

Data collection used a variable scan speed of 4.0–29.3° min^{-1} (2θ), a scan range of ($K\alpha_1-1$) to ($K\alpha_2+1$)° and a background/scan ratio of 0.5. The absorption correction was by the ψ-scan method and Lorentz and polarization corrections were applied. All calculations were carried out with the *SHELXTL/PC* (Sheldrick, 1990) system of programs on a 486 PC computer. Refinement was by full-matrix least squares with anisotropic displacement factors, a structure-factor weighting scheme and absolute configuration. H-atom positions were constrained so that O—H ≃ 0.98 Å by the addition of extra weighted observational equations to the least-squares matrix.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71721 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1039]

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Li_3NbO_4

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Abstract

A single crystal of trilithium niobate, Li_3NbO_4, was obtained for the first time by extraction from a LiCl flux. The structure comprises Nb_4O_{16} clusters, which form a body-centred cubic lattice, with Li ions located among the Nb_4O_{16} clusters. O ions coordinate to Nb and Li in an octahedral manner.

Comment

The structure of Li_3NbO_4 has been reported previously (Blasse, 1963). The structure determination, however, was carried out with a powder sample and the *R* factor was fairly large. Since a single crystal has been successfully obtained (Suzuki, Shishido, Ukei & Fukuda, 1993), the present study was carried out.

After submission of this manuscript, the authors were informed of a structural study of Li_3NbO_4 by neutron diffraction (Grenier & Bassi, 1965). The positional parameters from the earlier study are similar to those reported here, but the space group determined previously (*I*23) is incorrect.

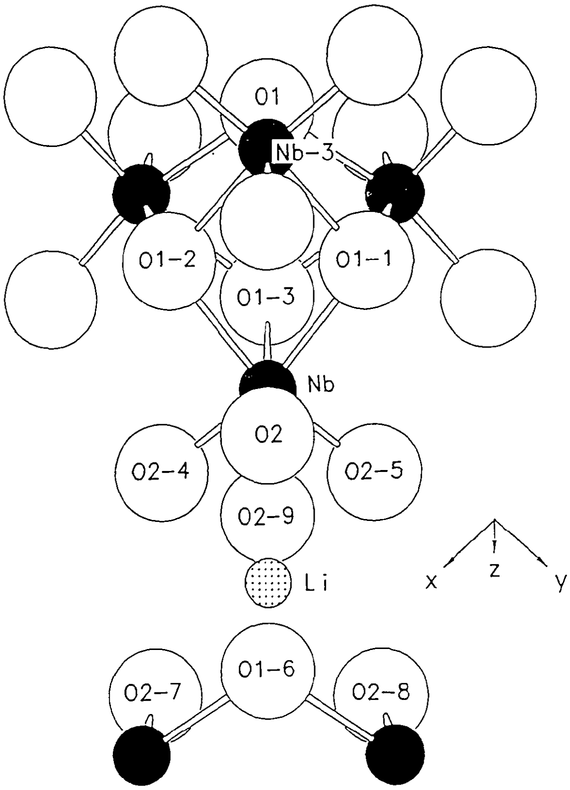

Fig. 1. A view of the Nb_4O_{16} cluster and a Li ion with coordinating O ions. Filled, dotted and open circles represent Nb, Li and O ions, respectively. Atomic nomenclature is abbreviated: for example, O1-2 represents O(1'').

Experimental

Crystal data

Li_3NbO_4
$M_r = 177.73$
Cubic
$I\bar{4}3m$
$a = 8.412$ (2) Å
$V = 595.2$ (4) Å^3

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 19 reflections
$\theta = 30.4\text{–}31.3^\circ$
$\mu = 3.69$ mm^{-1}