

Fig. 2. A view of the unit cell.

across the six-membered  $\text{Mo}_6\text{O}_{24}$  ring closely match the non-bonded  $\text{O}\cdots\text{O}$  separation in the  $\text{AsO}_3$  tetrahedron (2.86 Å), whereas the corresponding distances in the  $\text{Mo}_5\text{O}_{21}$  ring are too small to accommodate arsenate groups. The present study has indicated that this criterion is not so strict. Expansion of the  $\text{Mo}_5\text{O}_{21}$  ring and distortion of the arsenate tetrahedron make the  $\text{O}\cdots\text{O}$  distance 2.74 Å.

In the cations, the average N–C bond distance is 1.330 Å, the bond angles range from 119.6 to 120.5° as usual.

Fig. 2 shows the crystal structure. There are  $\text{NH}\cdots\text{O}$  and  $\text{OH}\cdots\text{O}$  hydrogen bonds among the cations,

Table 3. Hydrogen bonds

E.s.d.'s are ~0.004 Å.

Donor	Acceptor	$d(\text{Å})$	Donor	Acceptor	$d(\text{Å})$
N(1)	O(6)	2.895	N(4)	O(8)	2.985
N(1)	O(6')	2.904	N(5)	O(5')	2.867
N(2)	O(3)	2.862	N(5)	O(7')	3.008
N(2)	O(9 <sup>ii</sup> )	2.876	N(6)	O(4')	3.173
N(3)	O(11)	3.174	N(6)	O(12)	2.989
N(3)	O(11 <sup>iii</sup> )	2.912	O(12)	O(8)	2.941
N(4)	O(4)	2.880	O(12*)	O(8)	2.902

Symmetry code: (i)  $1-x, y, \frac{1}{2}-z$ ; (ii)  $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$ ; (iii)  $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$ ; (iv)  $1+x, -y, \frac{1}{2}+z$ ; (v)  $1+x, y, z$ ; (vi)  $1-x, -y, 1-z$ .

anions and water molecules. The hydrogen bonds are listed in Table 3. Each anion is surrounded by eight cations, and each cation has two anions as the first neighbours in the range 5.8–6.4 Å. The crystal is stabilized by Coulomb forces and hydrogen bonds.

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## Structure of $\text{ScBO}_3$

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**Abstract.** Scandium borate,  $M_r = 103.76$ , trigonal,  $R\bar{3}c$ ,  $a = 4.748(1)$ ,  $c = 15.262(2)$  Å,  $V = 298.0$  Å<sup>3</sup>,  $Z = 6$ ,  $D_x = 3.47$  g cm<sup>-3</sup>,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 33.95$  cm<sup>-1</sup>,  $F(000) = 300$ ,  $T = 298$  K,  $R = 0.017$  for 444 averaged reflections. The octahedral environment of O anions about the  $\text{Sc}^{\text{III}}$  ion exhibits a small

trigonal elongation, as demonstrated by the value of 92.28 (1)° for the bond angle O–Sc–O.

**Introduction.** As part of our program in new optical materials, we have recently synthesized and structurally characterized a number of new ternary and quaternary

borates containing the ion  $\text{Sc}^{\text{III}}$  (Sun, Thompson & Keszler, results to be submitted). To aid in our understanding and comparisons of the metrical details of these compounds and their spectroscopic features when doped with luminescent ions, we have determined the structure of the symmetric parent  $\text{ScBO}_3$ . When doped with the ion  $\text{Cr}^{\text{III}}$ , this material functions as a room-temperature near-infrared tunable laser (Lai, Chai, Long & Morris, 1986). The reported fluorescence lifetime of 115  $\mu\text{s}$  for the ion  $\text{Cr}^{\text{III}}$  in the laser material indicates that the environment of the  $\text{Sc}^{\text{III}}$  ion is only slightly distorted from  $O_h$  symmetry. The results of the structure determination are consistent with this result.

**Experimental.** Crystals of the title compound were grown from a melt composed of 14 mol %  $\text{ScBO}_3$  and 86 mol %  $\text{LiBO}_2$ . The solution was cooled at 8  $\text{K h}^{-1}$  from 1273 to 1023 K with subsequent removal of the solvent by dissolution in water. A crystalline block of dimensions 0.09  $\times$  0.08  $\times$  0.08 mm was used for data collection. Unit-cell parameters were derived from a least-squares analysis of the angle settings of 15 reflections in the range  $41 < 2\theta < 48^\circ$  that were automatically centered on a Rigaku AFC6R diffractometer. Intensity data were collected with the  $\omega$ - $2\theta$  scan technique; intensities of three standard reflections monitored throughout data collection exhibited an average fluctuation of 1.8%. From the 2228 reflections measured to  $(\sin\theta_{\text{max}})/\lambda = 1.22 \text{ \AA}^{-1}$  in the index range  $0 \leq h \leq 11$ ,  $-11 \leq k \leq 11$ ,  $-37 \leq l \leq 37$ , 444 unique data with  $F_o^2 \geq 3\sigma(F_o^2)$  were obtained.

All calculations were performed on a microVax II computer with programs from the *TEXRAY* crystallographic software package (Molecular Structure Corporation, 1985). The position of the Sc atom was derived by analogy with the calcite structure, with the remaining atomic positions determined from a difference electron density map. Following refinement with isotropic thermal parameters the data were corrected for absorption with the computer program *DIFABS* (Walker & Stuart, 1983) and subsequently averaged ( $R_{\text{int}} = 3.8$ ). Final refinement on  $F_o$  for those data having  $F_o^2 > 3\sigma(F_o^2)$  with 11 variables and 444 observations resulted in  $R = 0.017$ ,  $\Delta/\sigma = 0.48$ , and  $wR = 0.027$  where the weights are derived from counting statistics and a value of  $p = 0.05$ . The isotropic extinction parameter =  $7.4 \times 10^{-6}$  (Zachariasen, 1968) and  $S = 0.91$ . A maximum peak of  $0.46 \text{ e \AA}^{-3}$  is observed in the final difference electron density map, corresponding to 0.47% of a Sc atom. Fractional atomic coordinates and atomic displacement coefficients are given in Tables 1 and 2, respectively.\*

\* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44987 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

**Discussion.** The compound  $\text{ScBO}_3$  is reported to be the only thermodynamically stable compound in the system  $\text{Sc}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ , having a congruent melting point of 1883 K (Levin, 1967). From analysis of powder diffraction photographs it was predicted to be isostructural to the mineral calcite (Goldschmidt & Hauptmann, 1932). Analysis of precession photographs from single crystals grown from a flux of barium borate established the presence of trigonal symmetry and the space group  $R\bar{3}c$ , consistent with the calcite structure

Table 1. Positional parameters for  $\text{ScBO}_3$

	x	y	z
Sc	0	0	0
B	0	0	$\frac{1}{4}$
O	0.71038 (9)	0	$\frac{1}{4}$

Table 2. Anisotropic temperature coefficients for  $\text{ScBO}_3$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$B(\text{\AA}^2)$
Sc	0.00396 (8)	0.00396	0.00374 (6)	0.00198	0	0	0.307 (4)
B	0.0044 (3)	0.0044	0.0052 (3)	0.0022	0	0	0.37 (2)
O	0.00425 (9)	0.0059 (1)	0.0067 (1)	0.0029	-0.0008	-0.00165 (9)	0.43 (1)

From symmetry constraints  $U_{22} = U_{11}$ ,  $U_{12} = \frac{1}{2}U_{11}$ , and  $U_{13} = U_{23} = 0$  for the atoms Sc and B, and for the atom O,  $U_{12} = \frac{1}{2}U_{22}$  and  $U_{13} = \frac{1}{2}U_{23}$ ;  $B = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ .

Table 3. Bond distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) for  $\text{ScBO}_3$

Sc-O	2.1200 (4)	O-Sc-O	87.72 (1)
B-O	1.3752 (5)	O-Sc-O	92.28 (1)
		O-B-O	120
		Sc-O-Sc	123.78 (2)
		B-O-Sc	118.11 (1)

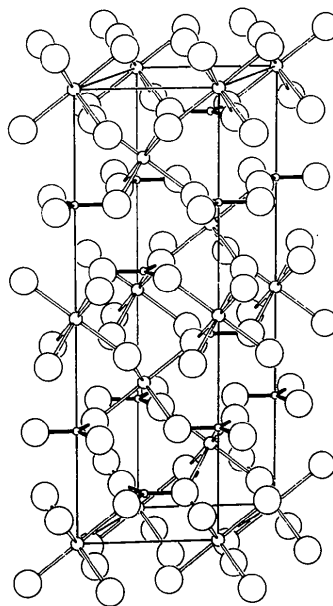


Fig. 1. Schematic ORTEP drawing (Johnson, 1965) of a unit cell of the compound  $\text{ScBO}_3$ . The largest circles represent O atoms and the smallest circles represent B atoms. The layers of planar  $\text{BO}_3$  groups extend orthogonal to the long, c axis.

(Biedl, 1966). The structure determination verifies these results, providing refined atomic parameters of high precision.

A drawing of the structure is given in Fig. 1. The general features of the structure are the same as those described for calcite (Megaw, 1973). Bond distances and bond angles are provided in Table 3. The bond distance, 1.3752 (5) Å, for the B—O interaction in the planar BO<sub>3</sub> group is comparable to similar bonding distances in the calcite-type materials AlBO<sub>3</sub>, 1.380 (Vegas, Cano & Garcia-Blanco, 1977), FeBO<sub>3</sub>, 1.379 (2) (Diehl, 1975), and LuBO<sub>3</sub>, 1.370 (3) Å (Abrahams, Bernstein & Keve, 1971). The angle O—Sc—O, 92.28 (1)°, demonstrates the small trigonal elongation of the octahedron of oxide ions about the Sc center. The distance Sc—O, 2.1200 (4) Å, compares with the distances 2.120 (1)—2.164 (1) Å for the two types of octahedrally coordinated Sc<sup>III</sup> ions in the compound Sc<sub>2</sub>O<sub>3</sub> (Knop & Hartley, 1968) and to similar distances, 2.07—2.17 Å, observed in the compound CaSc<sub>2</sub>O<sub>4</sub> (Müller-Buschbaum & Schnering, 1965). Only in ScPO<sub>4</sub> with the zircon structure where the Sc<sup>III</sup> ion occupies a distorted cube are dissimilar distances proposed, 2.09 and 2.37 Å (Mooney, 1956).

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## Structure de NaH<sub>2</sub>As<sub>3</sub>O<sub>9</sub>: un Nouvel Anion Arséniate Condensé

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**Abstract.** (NaH<sub>2</sub>As<sub>3</sub>O<sub>9</sub>)<sub>n</sub>, *M<sub>r</sub>* = 393.77, triclinic, *P* $\bar{1}$ , *a* = 7.167 (1), *b* = 7.575 (1), *c* = 7.850 (1) Å,  $\alpha$  = 109.89 (1),  $\beta$  = 107.27 (1),  $\gamma$  = 106.15 (1)°, *V* = 346.9 Å<sup>3</sup>, *Z* = 2, *D<sub>m</sub>* = 3.58, *D<sub>x</sub>* = 3.77 g cm<sup>-3</sup>, *F*(000) = 368,  $\lambda(\text{Mo } K\alpha)$  = 0.7107 Å,  $\mu$  = 142 cm<sup>-1</sup>, final *R* = 0.034 and *wR* = 0.039 for 1485 reflections with *F* >  $\sigma(F)$ . A new condensed arseniate anion is found. It consists of infinite (H<sub>2</sub>As<sub>3</sub>O<sub>9</sub>)<sub>n</sub><sup>-</sup> chains built from As<sub>4</sub>O<sub>14</sub> rings linked by bidentate bridging AsO<sub>4</sub> tetrahedra.

**Introduction.** L'établissement de la structure cristalline qui fait l'objet du présent article entre dans le cadre des travaux sur les arsénates condensés que nous avons entrepris. De plus, cette étude permettra de préciser la formule de ce composé caractérisé par Jouini & Guérin (1975) avec la formule dualistique Na<sub>2</sub>O.3As<sub>2</sub>O<sub>5</sub>.-2,25H<sub>2</sub>O. Toutefois, la précision des dosages chimiques et de l'analyse thermogravimétrique ne permettait pas d'avoir une certitude sur le nombre de molécules d'eau de la formule brute: 2 ou 2,25 H<sub>2</sub>O. Enfin la détermina-