chain lying in approximately the $(\bar{1}01)$ plane and oscillating about the (010) plane.

References

Hogg, J. H. C. & Sutherland, H. H. (1973). *Acta Cryst.* B29, 2483–2487.
Hogg, J. H. C. & Sutherland, H. H. (1976). *Acta Cryst.* B32, 2689–2690.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Sutherland, H. H., Hogg, J. H. C. & Walton, P. D. (1976). *Acta Cryst.* B32, 2539–2541.

The Crystal Structure of NaB₅O₆(OH)₄

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The synthetic compound $Na_2O.5B_2O_3.4H_2O$ is monoclinic, space group $P2_1/c$, with $a = 8.701$ (4), $b = 8.067$ (4), $c = 12.977$ (4) Å and $\beta = 106.77$ (2)°. The crystal structure was determined by means of direct methods from single-crystal X-ray diffractometer data. Refinement was carried out by least-squares calculations, yielding a final R value of 0.051. The basic structural unit is the isolated polyanion $|B_5O_6(OH)_4|$ formed by one tetrahedron and four triangles in the shape of a double hexagonal ring. The Na atom has six neighbours (three OH and three O) the four closest being arranged in a roughly tetrahedral configuration. The Na polyhedra connect B–O polyanions to form a three-dimensional network. Further connexions are provided by the hydrogen-bonding system. The structural formula is $NaB_5O_6(OH)_4$.

Introduction

The crystal study of the title compound is part of a systematic investigation of hydrated sodium borates (Corazza, Menchetti & Sabelli, 1974, 1975a,b).

One of the several phases obtained in the NaOH–B_2O_3–H_2O system under hydrothermal conditions at 150°C (Corazza, Menchetti, Sabelli & Stoppioni, 1977) has an X-ray powder pattern identical with the one that Nies & Hulbert (1967) assigned to sodium pentaborate dihydrate; that is the phase with $Na_2O:B_2O_3:H_2O$ molar proportions 1:5:4. In turn these authors pointed out that the 1:5:4 pattern is similar to that of the compound considered as 1:5:2 by Bouaziz (1962). However, Nies & Hulbert gave a different X-ray pattern to the compound with 1:5:2 oxide ratio and therefore there is a high probability that Bouaziz's pattern belongs to the 1:5:4 phase.

The present study confirms the composition found by Nies & Hulbert and allows the 1:5:4 compound to be classified among the soroborates with one tetrahedron and four triangles as the repeat unit. The structural formula is $NaB_5O_6(OH)_4$.

Experimental

Crystals of the compound were prepared at 150 ± 5°C, under hydrothermal conditions, by means of a pressure vessel supplied with temperature regulation and pressure read-out. Frequently the 1:5:4 phase was associated with H_3BO_3 and/or β-HBO_2. The crystals were rather large (up to 2 mm), but without well defined crystal forms, and were opaque. The unit-cell dimensions were determined from the scattering angles of 25 high-angle reflexions, measured with Mo $K\alpha$ radiation on a Philips single-crystal diffractometer. Systematic absences $l = 2n + 1$ in $h0l$ and $k = 2n + 1$ in $0k0$ uniquely indicate the space group $P2_1/c$. Crystal data are reported in Table 1.

Table 1. *Crystal data*

Na$|$B$_5$O$_6$(OH)$_4|$	$V = 872.1$ Å³
Space group: $P2_1/c$	Z 4
$a = 8.701$ (4) Å	$D_x = 2.178$ g cm⁻³
$b = 8.067$ (4)	FW 241.1
$c = 12.977$ (4)	μ(Mo $K\alpha$) – 2.79 cm⁻¹
$\beta = 106.77$ (2)°	$F(000)$ · 480

Intensity data were collected on a Philips four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy) from a small fragment of crystal, with Mo $K\alpha$ radiation and the ω–2θ scan technique. 1802 reflexions within the range $2° < \theta < 26.5°$ were inspected with a scan speed $0.04°$ s⁻¹ and scan range $1.2°$. The background was measured on both sides of the peak; for lower intensities scans were repeated up to three times. Of the 1802 reflexions scanned, 1291 were considered to be significant by the criterion $I > \sigma(I)$. Intensities were corrected for Lorentz–polarization effects. Because of the low absorption coefficient and the small size of the crystal no absorption correction was applied.

Structure determination and refinement

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). All 300 reflexions with $|E| > 1.38$ were included in the phase-determining process with eight sets of starting phases. On the first F_o-Fourier map all atoms were located with the exception of the H atoms, which were positioned by means of a ΔF Fourier synthesis.

Refinement was carried out by full-matrix least-squares techniques using first isotropic (R index from 0.30 to 0.21) and then anisotropic thermal parameters, to a final $R = 0.051$ for the 'observed' reflexions and $R = 0.079$ for all the data. Positional and thermal parameters of the H atoms were not refined. A weight $1/\sqrt{\sigma}$, with σ derived from counting statistics, was given

Table 2. *Atomic coordinates* ($\times 10^4$, *of the hydrogen atoms* $\times 10^3$) *and isotropic thermal parameters*

The B's of the non-hydrogen atoms are the equivalent ones, after Hamilton (1959).

	x	y	z	B (Å²)
Na	787 (2)	7601 (2)	2362 (1)	2.64
O(1)	4200 (3)	3160 (3)	3225 (2)	1.72
O(2)	3595 (3)	1603 (3)	4631 (2)	1.81
O(3)	1758 (3)	3693 (3)	3660 (2)	1.78
O(4)	981 (3)	1866 (3)	4872 (2)	1.85
O(5)	3017 (3)	3982 (3)	5556 (2)	2.08
O(6)	978 (3)	3515 (3)	6411 (2)	2.09
OH(7)	2789 (3)	5656 (3)	7009 (2)	2.44
OH(8)	−816 (3)	1345 (3)	5930 (2)	2.50
OH(9)	2432 (4)	5328 (4)	2370 (2)	2.52
OH(10)	5759 (3)	859 (3)	3947 (2)	2.26
B(1)	2816 (5)	4061 (5)	3103 (3)	1.71
B(2)	4524 (5)	1850 (5)	3957 (3)	1.76
B(3)	2339 (5)	2823 (5)	4689 (3)	1.64
B(4)	2291 (5)	4383 (5)	6306 (3)	1.78
B(5)	383 (5)	2218 (5)	5709 (3)	1.83
H(1)	380	600	705	4.0
H(2)	−100	40	560	4.0
H(3)	310	540	200	4.0
H(4)	595	0	445	4.0

to all the observed reflexions. No overall secondary extinction coefficient was applied, but during the last cycles of refinement three reflexions (100, 110 and 211) were excluded from calculations because they appeared to be affected by extinction.

The atomic scattering factors used in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1974). The positional and isotropic thermal parameters, along with their standard deviations, are given in Table 2.*

Discussion

The basic unit of the present structure is the isolated $[B_5O_6(OH)_4]^-$ polyanion, formed by one tetrahedron and four triangles in the shape of a double hexagonal ring. The packing of the B–O rings in the unit cell is shown in Fig. 1. According to Christ's (1960) third rule the hydroxyl O atoms are those linked to only one B; they are OH(7), OH(8), OH(9) and OH(10). As already observed, the H atoms were located on the basis of a difference Fourier synthesis.

The isolated pentaborate ion $[B_5O_6(OH)_4]^-$ was first found in the $KB_5O_6(OH)_4 \cdot 2H_2O$ compound (Zachariasen, 1937; Zachariasen & Plettinger, 1963). It was also described in the structure of β-$NH_4B_5O_6(OH)_4 \cdot 2H_2O$ (Merlino, 1969) and of sborgite, $NaB_5O_6(OH)_4 \cdot 3H_2O$ (Merlino & Sartori, 1972).

It is to be noted that, according to Christ's fourth rule, other structures have been found in which this polyanion is polymerized in various ways. In α-$K_2O \cdot 5B_2O_3$ (Krogh-Moe, 1971) as well as in the β-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32948 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
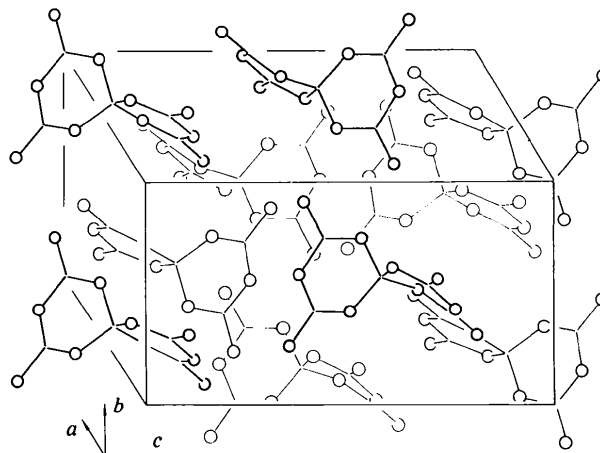

Fig. 1. The arrangement of some B–O polyanions in the structure. The unit cell is outlined.

modification (Krogh-Moe, 1965) the pentaborate group is part of a three-dimensional network with $[B_5O_8]^-$ as the repeat unit. A different polymerization is found in the mineral ammonioborite, $(NH_4)_3B_{15}$-$O_{20}(OH)_8.4H_2O$, where three double hexagonal rings are connected to give trimeric ions with the formula $[B_{15}O_{20}(OH)_8]^{3-}$ (Merlino & Sartori, 1971). In the mineral larderellite, $NH_4B_5O_7(OH)_2.H_2O$ (Merlino & Sartori, 1969), the polymerization of the pentaborate group leads to infinite chains with $[B_5O_7(OH)_2]^-$ as the repeat unit. From a compositional point of view larderellite is the ammonium analogue of the compound

Table 3. Na—O, B—O *bond distances*, B—B *distances and* O—O *edges* (Å) *of boron coordination polyhedra*

Na—O(3^i)	2·397 (5)
Na—OH(7^{ii})	2·383 (4)
Na—OH(8^{iii})	2·368 (3)
Na—OH(9)	2·324 (4)
Na—O(4^i)	2·924 (6)
Na—O(6^{iii})	2·668 (4)
Mean	2·511

B(1) triangle	
B(1)—O(1)	1·376 (5)
B(1)—O(3)	1·357 (6)
B(1)—OH(9)	1·370 (5)
Mean	1·368
O(1)—O(3)	2·389 (4)
O(1)—OH(9)	2·381 (4)
O(3)—OH(9)	2·335 (4)
Mean	2·368

B(2) triangle	
B(2)—O(1)	1·394 (5)
B(2)—O(2)	1·366 (6)
B(2)—OH(10)	1·342 (5)
Mean	1·367
O(1)—O(2)	2·395 (4)
O(1)—OH(10)	2·330 (4)
O(2)—OH(10)	2·378 (5)
Mean	2·368

B(3) tetrahedron	
B(3)—O(2)	1·489 (5)
B(3)—O(3)	1·464 (5)
B(3)—O(4)	1·486 (5)
B(3)—O(5)	1·451 (5)
Mean	1·473
O(2)—O(3)	2·413 (4)
O(2)—O(4)	2·393 (4)
O(2)—O(5)	2·393 (4)
O(3)—O(4)	2·391 (4)
O(3)—O(5)	2·399 (5)
O(4)—O(5)	2·435 (4)
Mean	2·404

B(4) triangle	
B(4)—O(5)	1·344 (6)
B(4)—O(6)	1·380 (5)
B(4)—OH(7)	1·359 (5)
Mean	1·361
O(5)—O(6)	2·378 (5)
O(5)—OH(7)	2·373 (4)
O(6)—OH(7)	2·316 (4)
Mean	2·356

B(5) triangle	
B(5)—O(4)	1·363 (5)
B(5)—O(6)	1·386 (5)
B(5)—OH(8)	1·356 (5)
Mean	1·368
O(4)—O(6)	2·400 (3)
O(4)—OH(8)	2·397 (5)
O(6)—OH(8)	2·309 (4)
Mean	2·369

Ring 1	
B(1)—B(2)	2·380 (6)
B(1)—B(3)	2·430 (6)
B(2)—B(3)	2·485 (5)
Mean	2·432

Ring 2	
B(3)—B(4)	2·457 (6)
B(4)—B(5)	2·380 (6)
B(3)—B(5)	2·487 (7)
Mean	2·441

Symmetry code

None	x	y	z		(iv)	$1-x$	$1-y$	$1-z$
(i)	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$		(v)	$-x$	$-y$	$1-z$
(ii)	x	$\frac{3}{2}-y$	$-\frac{1}{2}+z$		(vi)	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(iii)	$-x$	$1-y$	$1-z$		(vii)	$1-x$	$-y$	$1-z$

under investigation (1:5:4 for both phases) but the two structural arrangements are quite different.

The average B—O distances found in the above structures range from 1·359 to 1·373 Å in triangles and from 1·458 to 1·479 Å in tetrahedra. These mean values are not significantly different from each other, in spite of the various degrees of polymerization observed. Also the mean values found in the present investigation (1·366 Å in triangles and 1·473 Å in the tetrahedron) fall within the limits previously mentioned. Bond lengths are listed in Table 3.

In the 1:5:4 structure, however, some relevant differences in the individual B—O bond lengths are present; for instance B(4)—O(5), 1·344 Å (triangle), and B(3)—O(5), 1·451 Å (tetrahedron), are shorter than the mean values. The strengthening of the related bonds is clearly in the right direction to remove, in part at least, the electrostatic imbalance of O(5) which is not linked to the Na atom. As already pointed out by other authors, there is a noticeable difference between bond distances involving O atoms linked to one 'triangular' B and bond distances involving O atoms 'bridging' two triangular B atoms. In the present structure the two values are 1·357 and 1·384 Å respectively. This well known feature in B—O bond lengths can be explained, in part at least, in terms of π-bond order. A more complete explanation, however, cannot omit the whole structural arrangement: in the present case, for instance, the influence of the Na—O bonds is to be accounted for. From the O—B—O angles, reported in Table 4, one can deduce that the triangles are rather distorted. The two hexagonal rings are almost perpendicular to each other, the angle between the planes

Table 4. *Bond angles* (°)

O(3)—Na—OH(7^{ii})	106·7 (1)		O(1)—B(1)—O(3)	121·9 (3)
O(3)—Na—OH(8^{iii})	98·3 (1)		O(1)—B(1)—OH(9)	120·2 (4)
O(3)—Na—OH(9)	139·6 (1)		O(3)—B(1)—OH(9)	117·8 (3)
OH(7^{ii})—Na—OH(8^{iii})	99·0 (1)			
OH(7^{ii})—Na—OH(9)	89·0 (1)		O(1)—B(2)—O(2)	120·4 (3)
OH(8^{iii})—Na—OH(9)	116·0 (1)		O(1)—B(2)—OH(10)	116·7 (4)
			O(2)—B(2)—OH(10)	122·9 (3)
O(3^i)—Na—O(4^i)	52·3 (1)			
O(3^i)—Na—O(6^{iii})	81·6 (1)		O(5)—B(4)—O(6)	121·7 (3)
OH(7^{ii})—Na—O(4^i)	97·7 (1)		O(5)—B(4)—OH(7)	122·9 (4)
OH(7^{ii})—Na—O(6^{iii})	153·1 (1)		O(6)—B(4)—OH(7)	115·5 (4)
OH(8^{iii})—Na—O(4^i)	149·5 (1)			
OH(8^{iii})—Na—O(6^{iii})	54·2 (1)		O(4)—B(5)—O(6)	121·7 (3)
OH(9)—Na—O(4^i)	89·5 (1)		O(4)—B(5)—OH(8)	123·7 (3)
OH(9)—Na—O(6^{iii})	101·0 (1)		O(6)—B(5)—OH(8)	114·7 (4)
O(4^i)—Na—O(6^{iii})	107·1 (1)			
			O(2)—B(3)—O(3)	109·6 (3)
Ring 1			O(2)—B(3)—O(4)	107·1 (3)
B(1)—O(1)—B(2)	118·5 (3)		O(2)—B(3)—O(5)	109·0 (2)
B(2)—O(2)—B(3)	121·0 (3)		O(3)—B(3)—O(4)	108·3 (2)
B(3)—O(3)—B(1)	118·9 (3)		O(3)—B(3)—O(5)	110·8 (3)
			O(4)—B(3)—O(5)	112·0 (3)
Ring 2				
B(3)—O(5)—B(4)	123·1 (3)			
B(4)—O(6)—B(5)	118·8 (3)			
B(5)—O(4)—B(3)	121·6 (3)			

Table 5. *Displacements of other atoms from the planes of ring oxygens; dihedral angles in the polyanion*

|	Ring 1	Ring 2
Ring oxygen atoms	O(1), O(2), O(3)	O(4), O(5), O(6)
Associated atoms	B(1) 0·07 Å	B(3) −0·13 Å
	B(2) −0·12	B(4) −0·05
	B(3) 0·41	B(5) 0·08
	O(4) −0·33	O(2) 0·97
	O(5) 1·84	O(3) −1·42
	OH(9) 0·14	OH(7) −0·15
	OH(10) −0·37	OH(8) 0·24
Angle between rings		86·8°
Oxygen atoms of triangle	O(1), O(3), OH(9)	O(5), O(6), OH(7)
Triangle–ring angle	4·1°	4·2°
Oxygen atoms of triangle	O(1), O(2), OH(10)	O(4), O(6), OH(8)
Triangle–ring angle	10·4°	6·8°

Table 6. *Hydrogen-bonding system with related distances (Å) and angles (°)*

Donor atom (D)	H	Acceptor atom (A)	D···A	D–H	H···A	∠D–H···A
OH(7)	H(1)	O(1ⁱᵛ)	2·885 (4)	0·91	1·99	167
OH(8)	H(2)	O(4ᵛ)	2·780 (4)	0·87	1·93	167
OH(9)	H(3)	OH(10ᵛⁱ)	2·670 (6)	0·86	1·83	168
OH(10)	H(4)	O(2ᵛⁱⁱ)	2·659 (4)	0·93	1·73	177

Table 7. *Electrostatic valence balance*

	Na	B(1)	B(2)	B(3)	B(4)	B(5)	H_{don}	H_{acc}	Sums
O(1)		0·98	0·93					0·17	2·08
O(2)			1·00	0·72				0·23	1·95
O(3)	0·19	1·03		0·77					1·99
O(4)	0·06			0·72		1·02		0·19	1·99
O(5)				0·79	1·05				1·84
O(6)	0·11				0·94	0·95			2·00
OH(7)	0·20				1·01		0·83		2·04
OH(8)	0·21					1·03	0·81		2·05
OH(9)	0·23	0·99					0·77		1·99
OH(10)			1·07				0·77	0·23	2·07
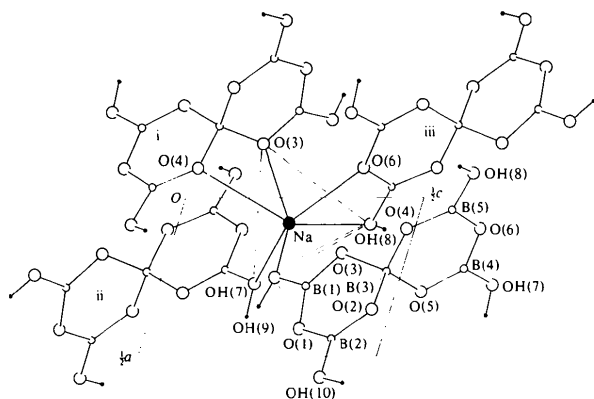
Fig. 2. The *ac* projection of the structure. Broken lines indicate the 'tetrahedron' around the Na atom.

defined by O(1), O(2), O(3) and by O(4), O(5), O(6) being 86·8°. Other information on the mean planes and the deviations of atoms from these planes are given in Table 5.

Within the limit 3·30 Å the Na atom has six neighbours (three OH and three O) whose distances from the cation fall in two well-separated ranges. The four closest atoms show a roughly tetrahedral configuration (see Fig. 2) and a mean distance of 2·368 Å, the other two distances being 2·668 and 2·924 Å respectively (see Table 3). In the literature there are some other examples of structures in which the Na atom is in a so-called tetrahedral coordination or with four short Na—O distances and other distances remarkably longer. Na—O bond distances found in eight such structures are compared in Fig. 3 with those
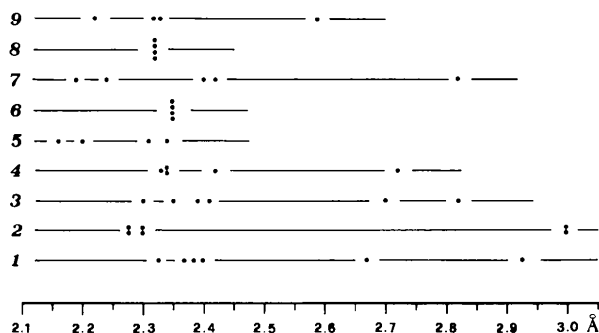
Fig. 3. Plot of Na—O bond distances observed in structures with Na in 'tetrahedral' coordination. (1) $NaB_3O_6(OH)_4$ (present study). (2) Sborgite, $NaB_5O_6(OH)_4.3H_2O$ (Merlino & Sartori, 1972). (3) $NaOH.H_2O$ (Wunderlich, 1957). (4) $Na_2Mn_2Si_2O_7$ (Astakhova & Simonov, 1969). (5) β-$NaFeO_2$ (Bertaut & Blum, 1954). (6) $Na_5Lu(WO_4)_4$ (Klevtsova, Glinskaya, Kozeeva & Klevtsov, 1972). (7) $Na_2Zr(SO_4)_3.3H_2O$ (Bear & Mumme, 1971). (8) Na_2PtO_2 (Urland & Hoppe, 1972). (9) $Na_5P_3O_{10}$ (Corbridge, 1960).

found in the structure of the 1:5:4 phase. The splitting of values into two well-separated ranges is evident. The overall mean Na—O value for the short distances is 2·331 Å; with the exception of one value (2·59 Å), there is a blind region from 2·42 to 2·67 Å. On the other hand, the O—Na—O angles show such a wide range of values that it is difficult to describe the Na coordination as tetrahedral. As shown in Table 4, in the 1:5:4 structure the 'tetrahedral' angles range from 89·0 to 139·6°.

The Na polyhedra are not directly linked to each other, but connect B—O polyanions to form a three-dimensional network. In fact each Na atom links, with short distances, four O atoms belonging to four B—O polyanions and two more O atoms (with longer distances) belonging to two of the four previous B—O double rings; in this way each B—O polyanion is connected to four neighbouring Na atoms. Further connexions are provided by the four independent H bonds. Distances and angles related to the hydrogen-bonding system are reported in Table 6.

An electrostatic valence balance, computed according to the method of Brown & Shannon (1973), is shown in Table 7. The balance is quite satisfactory for all the O atoms with the exception of O(5) which is not linked to the Na atom and does not receive hydrogen bonds.

References

ASTAKHOVA, L. P. & SIMONOV, V. I. (1969). Kristallografiya, 14, 3–8.

BEAR, I. J. & MUMME, W. G. (1971). Acta Cryst. B27, 494–500.

BERTAUT, F. & BLUM, P. (1954). C.R. Acad. Sci. 239, 429–431.

BOUAZIZ, R. (1962). Bull. Soc. Chim. Fr. pp. 1451–1456.

BROWN, J. D. & SHANNON, R. D. (1973). Acta Cryst. A29, 266–282.

CHRIST, C. L. (1960). Am. Mineral. 45, 334–340.

CORAZZA, E., MENCHETTI, S. & SABELLI, C. (1974). Am. Mineral. 59, 1005–1015.

CORAZZA, E., MENCHETTI, S. & SABELLI, C. (1975a). Acta Cryst. B31, 1993–1997.

CORAZZA, E., MENCHETTI, S. & SABELLI, C. (1975b). Acta Cryst. B31, 2405–2410.

CORAZZA, E., MENCHETTI, S., SABELLI, C. & STOPPIONI, A. (1977). Neues Jahrb. Mineral. Abh. To be published.

CORBRIDGE, D. E. C. (1960). Acta Cryst. 13, 263–269.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). Acta Cryst. A27, 368–376.

HAMILTON, W. C. (1959). Acta Cryst. 12, 609–610.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

KLEVTSOVA, R. F., GLINSKAYA, L. A., KOZEEVA, L. P. & KLEVTSOV, P. V. (1972). Sov. Phys. Crystallogr. 17, 672–676.

KROGH-MOE, J. (1965). Acta Cryst. 18, 1088–1089.

KROGH-MOE, J. (1971). Acta Cryst. B28, 168–172.

MERLINO, S. (1969). Atti Accad. Naz. Lincei Cl. Sci. Fis. Mat. Nat. Rend. Ser. VIII, 47, 85–99.

MERLINO, S. & SARTORI, F. (1969). Acta Cryst. B25, 2264–2270.

MERLINO, S. & SARTORI, F. (1971). Science, 171, 377–379.

MERLINO, S. & SARTORI, F. (1972). Acta Cryst. B28, 3559–3567.

NIES, N. P. & HULBERT, R. W. (1967). J. Chem. Eng. Data, 12, 303–313.

URLAND, W. & HOPPE, R. (1972). Z. Anorg. Chem. 392, 23–36.

WUNDERLICH, J. A. (1957). Acta Cryst. 10, 462–463.

ZACHARIASEN, W. H. (1937). Z. Kristallogr. 98, 266–274.

ZACHARIASEN, W. H. & PLETTINGER, H. A. (1963). Acta Cryst. 16, 376–379.