of its high-temperature origin. The shortest Fe—Fe interaction [3·1023 (8) Å] is found between $M(12)$ and $M(25)$; in orthoferrosilite it is only 2·9938 (7) Å (Seifert & Weber, 1982). The SiO_4 tetrahedra, which link the octahedral bands zipper-like, display an almost steady increase in the degree of their distortion as manifested in their bond-angle variance, from 19·6 deg^2 for Si(1) to 47·8 deg^2 for Si(9). This feature is found in all pyroxenoids and may be caused by an increasing out-of-registry of the octahedra from neighbouring bands which are linked by the Si atoms. As observed in all other pyroxenoids the cation at the $M(22)$ site is shifted far off-center and has an abnormally large amplitude of vibration. In the case of ferrosilite III, the only pyroxenoid where the temperature factors have been refined anisotropically, the ellipsoid of thermal motion is unusually anisotropic and the axis of its largest amplitude points to the center of the octahedral face towards which the atom has been displaced; this is roughly towards the more remote [2·879 (2) Å] of the two O(B1) oxygen atoms. Whether the potential at this site is of an anharmonic or a double-well nature will be discussed in a forthcoming publication, which will also deal with the electron distribution within the present compound.

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Structure of Basic Sodalite, $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$

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Abstract. $M_r = 968·34$, cubic, $P\bar{4}3n$, $a = 8·890$ (1) Å, $V = 702·6$ (1) Å^3, $Z = 1$, $D_x = 2·29$ Mg m^{-3}, $F(000) = 480$, graphite-monochromatized Mo $K\alpha$ radiation, $\lambda K\alpha_1 = 0·71069$Å, $\mu = 0·775$ mm^{-1}. Final $R = 0·022$ for 152 observed reflexions. The 1:1 alumino-silicate framework is completely ordered whereas the O of the hydroxyl group and water molecule is disordered about the body diagonal of the cubic cell due to spatial requirements and the presence of hydrogen bonds; thus only four of the 24(i) cavity O positions can be occupied simultaneously and the chemical formula above is ideal.

Introduction. Basic sodalite is isotypic with sodalite $Na_8Al_6Si_6O_{24}Cl_2$ (Pauling, 1930) and polymorphic with basic cancrinite (Pahor, Calligaris, Nardin & Randaccio, 1982) the latter being the low-temperature polymorph (Anderson & Burley, 1982). Zeolites are distinguished on the basis of their structural type (Meier & Olsen, 1971) which is defined by the topology of their alumino-silicate frameworks. Accordingly, basic sodalite and basic cancrinite may be considered members of the zeolite family. As in the zeolites, these minerals contain interframework ions which can be replaced without disrupting the framework bonds. Basic sodalite is stable at higher temperatures than other zeolites and therefore offers a means of gas storage at these higher temperatures, with possible controlled release of the gas (Barrer & Vaughan, 1971).

Bukin & Makarov (1967) reported a single-crystal neutron diffraction structure of a synthetic basic sodalite $Na_{7·1}Al_6Si_{5·5}H_{0·5}Cl_{0·4}(OH)_{0·7}.0·7H_2O$, space group $P\bar{4}3n$ and $a = 8·887$ Å. They found that $\frac{1}{12}$ of the Si atoms were replaced by four H atoms arranged in tetrahedral fashion on the midway point of the O—O edges of the original SiO_4 tetrahedron, giving an H_4O_4

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tetrahedral grouping. They did not locate the 0·7 H_2O shown by the chemical analysis and the OH group was placed in the vacant Na site. Subsequently a PMR study on a similar hydroxyl-bearing sodalite (Galitskii, Shcherbakov & Gabuda, 1973) failed to find H_4O_4 groups. They indicated that the O of the OH and H_2O groups occupied the 8(*e*) position in space group $P\bar{4}3n$ ($x = 0{\cdot}83$). This was confirmed by Galitskii, Shcherbakov & Gabuda (1974) using the NMR spectra of ^{23}Na. They suggested an idealized formula for basic sodalite of $Na_8Al_6Si_6O_{24}(OH)_2.6H_2O$.

Experimental. Prepared hydrothermally, 1·55 TPa total pressure, 723K, dodecahedral form (Anderson & Burley, 1982), 0·17 × 0·20 × 0·23 mm, chemical analysis (wet analysis, J. Muysson, McMaster University) (wt.%) SiO_2 37·38, Al_2O_3 32·09, Na_2O 25·35, H_2O 5·50, total 100·32, calculated cell contents (based on Al + Si = 12) Si 5·97, Al 6·03, Na 7·84, H_2O 1·92, OH^- 1·92, precession photographs show sharp reflexions and no superstructure, symmetry consistent with space group $P\bar{4}3n$ with *hhl, lhh* and *hlh* absent when $l \neq 2n$, cell parameter determined by least-squares, 20 reflexions, automatic four-circle single-crystal diffractometer; all reflexions (1570) collected in the octant with *h, k* and *l* positive out to a maximum 2θ of 65°, Nicolet P3 four-circle diffractometer, θ–2θ scan mode, 2θ scan range ($K\alpha_1 - 0{\cdot}85°$) to ($K\alpha_2 + 0{\cdot}85°$), variable scan rates of 3 to 29·3° min^{-1}, dependent on the intensity of a prescan, three standard reflexions monitored after every 50 reflexions did not change; Lorentz, polarization, background effects and spherical absorption ($\mu R = 0{\cdot}16$) corrections, equivalent reflexions averaged to produce a unique set; all crystallographic calculations made using XRAY 76 (Stewart, 1976).[*]

Initial positional parameters and isotropic temperatures factors were those of sodalite (Hassan & Grundy, 1982), atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). A full-matrix least-squares technique was used to refine the atomic positions and isotropic temperature parameters of the framework atoms [Si, Al and O(1)] and Na, with a variable overall scale factor and unit weights. This converged to $R = 0{\cdot}048$, with geometry comparable to that found in sodalite. The temperature factors of these atoms were normal, except that of Na which was significantly larger than that observed for sodalite, as was the Na–O(1) distance. Initially, the O of the OH and H_2O groups [O(2)] was placed at the 8(*e*) position with $x = 0{\cdot}9$, based on an estimated value of 2·38 Å for the Na–O(2) distance. This position refined to $x = 0{\cdot}9191$ with $U_{\text{iso}} = 0{\cdot}110$ Å^2. Refinement of the populations of the Na and O(2) sites was consistent with the chemical analysis, with the Na site full and the O(2) site half occupied. The isotropic model was then converted to the anisotropic form and converged to $R = 0{\cdot}026$. A final difference Fourier map was featureless; in particular there was no evidence of an atom on the 2(*a*) position which is occupied by Cl in sodalite.

Interatomic distances and bond-valence sums about each atom (Brown & Shannon, 1973) pertinent to this trial structure are included in Table 2. The Al and Si ions are charge balanced and therefore the Si–O and Al–O distances are indicative of complete ordering of the framework, which further justifies the choice of space group. The framework O(1) has a bond-valence sum of approximately 2 v.u. as expected, whereas the Na bond-valency deficiency of ~ 0·09 v.u. for this trial structure requires that there be $\frac{3}{4}$ O(2) per site (*i.e.* three per cavity), which is too much according to the chemical analysis. Furthermore, the O(2)–O(2) nonbonded distance of 2·034 Å is unrealistically short. From the chemical analysis, each framework cavity contains one OH^- and one H_2O, and thus the hydrogen-bonding interaction cannot be symmetrical; also, O(2) has unusually large temperature parameters and a thermal ellipsoid which is elongated in the Na–O(2) bond direction. These observations suggest that O(2) is displaced off the cube diagonal to a general 24(*i*) position, as was found in cancrinite (Grundy & Hassan, 1982). Further refinement with O(2) disordered on the 24(*i*) position and the site-occupancy constrained by the chemical analysis converged to $R = 0{\cdot}022$ and $R_w = 0{\cdot}026$ for 152 observed reflexions with $|F| > 3\sigma(F)$. The refinement was repeated with all 310 reflexions treated as observed which gave $R = 0{\cdot}049$ and $R_w = 0{\cdot}045$ with no significant change in parameters. The location of H could not be determined experimentally. The final parameters are given in Table 1.

Discussion. The general features of the sodalite structure have been described elsewhere (Pauling, 1930) so that only details pertaining to this study will be given. The cavity is occupied by four Na atoms, one OH and one H_2O. Twelve of the possible 24 O(2) positions are within a single cavity which is not large enough to allow occupancy of more than two of these positions, based

Table 1. *Atomic positional parameters and isotropic thermal parameters* (Å^2 × 10^4) *with e.s.d.'s in parentheses*

	Occupancy	Site	x	y	z	U_{iso}
Na	1·0	8(*e*)	0·1755 (2)	0·1755	0·1755	281 (8)
Si	1·0	6(*c*)	$\frac{1}{4}$	$\frac{1}{2}$	0	81 (7)
Al	1·0	6(*d*)	$\frac{1}{4}$	0	$\frac{1}{2}$	83 (8)
O(1)	1·0	24(*i*)	0·1397 (4)	0·1506 (4)	0·4399 (3)	134 (5)
O(2)	0·17	24 (*i*)	0·0704 (64)	0·1178 (35)	−0·0526 (50)	491 (77)

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38085 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

on observed hydrogen-bonded O—O contact distances (Table 1 of Brown, 1976). This is consistent with the lack of superstructure and the refined O(2) occupancy of 0·17 atoms per site; the space-group symmetry requires a completely disordered O(2)—O(2) configuration within the cavity.

We can also analyse the cavity contents using bond valence. Each non-framework O is statistically coordinated to three Na atoms at distances of 2·29, 2·50 and 2·98 Å. Using the universal curves of Brown & Shannon (1973), each O contributes 0·445 v.u. to the Na (Table 2). The total bond-valence requirement of the cavity Na atoms from non-framework O is approximately 1 v.u., which corresponds to two O atoms. The ideal chemical composition of basic sodalite is therefore $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$, with the two cavity O atoms bridged by a symmetrical hydrogen bond and each having a further weak hydrogen bond to the framework O which determines its final location.

Table 2. *Selected bond distances* (Å), *angles* (°) *and valence sums with e.s.d.'s in parentheses*

SiO_4 tetrahedra		
Si–O(1)	4 × 1·616 (4)	Si = 4 × 1·019 (10)
O(1)–O(1)	4 × 2·604 (5)	= 4·076 (21) v.u.
	2 × 2·705 (5)	
O(1)–Si–O(1)	4 × 107·4 (2)	
	2 × 113·6 (2)	
AlO_4 tetrahedra		
Al–O(1)	4 × 1·743 (4)	Al = 4 × 0·734 (7)
O(1)–O(1)	4 × 2·829 (5)	= 2·936 (14) v.u.
	2 × 2·883 (6)	
O(1)–Al–O(1)	4 × 108·4 (1)	
	2 × 111·6 (2)	
Si–O(1)–Al	138·7 (2)	
Sodium coordination		
Na–O(1)	3 × 2·382 (3)	Na = 3 × 0·194 (1)
–O(1)	3 × 3·079 (3)	+ 3 × 0·046 (1)
Na–O(2)	3 × 2·291 (46)	+ 0·17 × 3 × 0·241 (29)
	3 × 2·496 (54)	+ 0·17 × 3 × 0·148 (19)
	3 × 2·977 (36)	+ 0·17 × 3 × 0·056 (3)
		= 0·947 (35) v.u.
Oxygen coordination		
O(1)–O(2)	3·287 (48)	O(1) = 1·019 (10) + 0·734 (7) + 0·194 (1)
		= 1·947 (12) + 0·046 (1) = 1·993 (12) v.u.
–O(2)	3·410 (37)	O(2) = 0·241 (29) + 0·148 (19) + 0·056 (3)
		= 0·445 (35) v.u.
–O(2)	3·425 (41)	
O(2)–O(2)	2·440 (56)	
Results of trial structure refinement with O(2) at 8(*e*)		
Sodium coordination		
Na–O(1)	3 × 2·382 (3)	Na = 3 × 0·194 (1) + 3 × 0·0461 (1)
–O(1)	3 × 3·079 (3)	+ 0·5* × 3 × 0·126 (8)
Na–O(2)	3 × 2·571 (30)	= 0·909 (14) v.u.
Oxygen coordination		
O(1)–O(2)	3 × 3·451 (25)	O(2) = 3 × 0·126 (8)
O(2)–O(2)	3 × 2·034 (47)	= 0·378 (14) v.u.

* Population based on chemical analysis.

It is likely at high temperatures, that expansion will allow three O atoms into the cavity. However, it is highly improbable that this expansion would be great enough to accommodate more than three O atoms prior to melting. Therefore, depending on the rate of diffusion of H_2O from the structure on cooling we can expect a range of composition from $Na_8Al_6Si_6O_{24}(OH)_2.2H_2O$ to $Na_8Al_6Si_6O_{24}(OH)_2.4H_2O$. An increase in the size of the cell parameter should reflect the presence of water in excess of two molecules.

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