

The crystal structures of aluminosilicate-sodalites: X-ray diffraction studies and computer modelling

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ABSTRACT. X-ray powder methods have been used to study the room-temperature structures of the synthetic sodalites: $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, $\text{K}_{7.6}\text{Na}_{0.4}(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, and $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$. Natural sodalite was also studied and the atomic coordinates show satisfactory agreement with those determined from the single-crystal data of Löns and Schulz (1967). The LiCl- and KCl- as well as the NaCl-sodalites refined in the expected sodalite space group $P\bar{4}3n$, but the NaI-sodalite fitted $I\bar{4}3m$ better. The resulting structural data reveal shortcomings in the previous computer models for sodalite structures and an improved computer modelling procedure is devised which successfully predicts atomic coordinates, starting from the experimental a value and an estimate of the cation-anion distance. The method incorporates the experimental result that the average T -O distance ($T = \text{Al}, \text{Si}$) throughout the samples is $\sim 1.678 \text{ \AA}$, and Si-O and Al-O are set at 1.618 and 1.738 \AA , respectively. Although T -O remains little changed throughout the samples, the data confirm the inverse relationship between $\angle T$ -O- T and the tetrahedron tilt angle ϕ , in which $\angle T$ -O- T approaches $\sim 160^\circ$ as $\phi \rightarrow 0^\circ$ and the sodalite cage becomes fully expanded.

PREVIOUS work on members of the sodalite family (Henderson and Taylor, 1977, 1979a; Taylor and Henderson, 1978; Dempsey and Taylor, 1980) has been directed towards: (i) understanding the nature of the bonding in framework structures, particularly in respect of T -O distances and T -O- T angles ($T = \text{Al}, \text{Si}$); (ii) interpreting the infra-red spectra of framework structures and; (iii) interpreting the thermal expansion behaviour of framework structures. However, each of the studies, to which reference has been made, encountered problems which could not be resolved without more structural data for sodalites, particularly aluminosilicate-sodalites.

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The structural data required include T -O distances, T -O- T angles and tilt angles ϕ for aluminosilicate-sodalites showing a wide range of cell edge and hence a wide degree of structural collapse (for nomenclature see Taylor, 1972, and Dempsey and Taylor, 1980). Such a range of aluminosilicate-sodalites is available, in powder form, from earlier studies (Henderson and Taylor, 1977). From these powder samples, $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, $\text{K}_{7.6}\text{Na}_{0.4}(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, and $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$ were selected for the present X-ray structural study. The structure of natural sodalite, $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, has already been determined by Pauling (1930) and refined by Löns and Schulz (1967) who used single-crystal data, but this mineral was included in the present study to check the correspondence of powder and single crystal results.

Once the powder studies were complete, it proved possible to develop a computer model enabling structural details to be calculated for each sodalite simply from its unit-cell parameter a .

Experimental procedure. The specimen of $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ was a natural one, No. 19 of Taylor (1967); the remaining specimens were the synthetic sodalites used in an earlier infra-red study (Henderson and Taylor, 1977). Each powdered specimen was packed into a glass capillary, 0.3 mm internal diameter, and a powder X-ray diffraction film produced using Cu-K_α radiation and a Philips 114 mm diameter powder camera (Ievins-Straumanis film mounting). To obtain intensity measurements each film was scanned at 0.05 mm intervals along the axis of the diffraction pattern using an automated Joyce-Loebl microdensitometer. Digitized data obtained on punched paper tape were loaded into computer files on the joint ICL 1906A/CDC 7600 computer system of the University of Manchester Regional Computer Centre and processed by programmes in our *MO*Lecular structure programme *Library*(MOLLY) to optical density read-

ings at each step. Reflection peak areas were determined by integration from the computer output and an average taken of corresponding reflections on the two halves of the X-ray pattern. The reflections were divided into unique and non-unique sets. The intensity of each non-unique reflection (a composite made up of components with different Miller indices hkl) was split into the intensities of its components in proportion to the ratios of the intensities of the components calculated from an initial estimate of the crystal structure (Beagley *et al.*, 1982). At stages through the structure refinement, the ratios of the intensities of the components of the non-unique reflections were redetermined from the partially-refined parameters and used to re-divide the intensities of the non-unique reflections into their component reflections.

Because of the difficulty of determining space groups from powder diffraction data, in preliminary least-squares refinements of structural parameters it was initially assumed that all the structures had the space group of the mineral sodalite, $P43n$. The atomic scattering factors used were for Si^{2+} , Al^+ , O^- , Na^+ , Li^+ , K^+ , Cl^- , and I^- (International Tables, 1974). Factors for partially ionized Si, Al, and O were used to make some allowance for covalency in the tetrahedral framework. Each unique reflection was given unit weight. The weight given to each component of a non-unique reflection was the reciprocal of the number of components making up that non-unique reflection, thereby giving unit weight, in total, to each non-unique reflection. The calculated linear absorption coefficients for the specimens were reduced by 30% to make an approximate allowance for the pore space present in the specimen in the capillary. Isotropic temperature factors were employed for each atom. Initially, separate scale factors were used for the unique and non-unique reflections, although if the method of processing the latter succeeds they should be equal. In fact, the individual scale factors were not significantly different so that ultimately a single factor was used. The structural determinations and refinement were carried out using the X-ray Systems, Version of June 1972 (Technical Report TR-192 of the Computer Science Center, University of Maryland, USA, June 1972). Because of correlation effects the isotropic temperature factors of the Si and Al atoms could not be refined separately and so were refined together.

$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$ did not refine coherently in space group $P43n$. During refinement, the coordinates of the oxygen atom moved to x, x, z rather than x, y, z and the F_0 map in the region of the oxygen atom supported this relationship. The equality of x and y shows that the Al, Si-O bond lengths are equal suggesting that the Si and Al sites are disordered and that the space group is $I43m$. The structure refined more smoothly in $I43m$ and the agreement with experiment remained the same as for $P43n$. The criteria of Hamilton (1965) support the adoption of $I43m$ because no reduction in the appropriate residual is observed in the $P43n$ refinement although there is one extra variable. The isotropic temperature factors for all the atoms in the I-sodalite structure were much higher than those for the other sodalites with ordered frameworks.

The single-crystal structural data of Löns and Schulz

(1967) for natural sodalite were also refined using the X-ray System 1972, for comparison with our own structural analysis of powdered $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$.

Results. Bond distances and angles for the sodalites studied are given in Table I. Unit cell parameters a , atomic coordinates, isotropic temperature factors, etc., are given in Table II. We have chosen to present the data in this order so as to facilitate comparison of measured atomic parameters with those estimated using the model.

For natural sodalite [$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$], the atomic parameters of Löns and Schulz (1967) are not significantly different from those of our own refinement (Table II) using their data except for the x -coordinate of the oxygen atom (z of Löns and Schulz, 1967; note that x, y, z here are a cyclic permutation of those of Löns and Schulz). This slight difference, which results in shorter Si-O and longer Al-O distances, may result from the use of a different set of scattering factors and a different refinement programme. The results of the refinement using our powder data for natural sodalite are in fair agreement (generally slightly greater than 2σ) with the results for the single crystal determination (Table IIb and Table I, columns 2 and 3). These refinements demonstrate that the powder studies are reasonably reliable.

The structures of $\text{Li}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$, $\text{K}_{7.6}\text{Na}_{0.4}(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$ and $\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{I}_2$ have not been determined previously although they have been modelled by Taylor and Henderson (1978) and Dempsey and Taylor (1980). The C-A and C-O distances calculated by the latter authors are given in Table I for comparison with the observed values (C = cavity cation, A = cavity anion). In all cases (except that of the single crystal data, which had been used as a constraint on the model) the model C-O distances are smaller than the corresponding observed values, and the model C-A distances are greater than observed, particularly for the lithium sodalite. This suggests that the model calculations give poor cation coordinates. The model C-O distances which fix the cation coordinates, had been calculated as the sum of ionic radii, and it is clear that this is a feature of the earlier modelling which is unsatisfactory. Furthermore, the model calculations recognized only three oxygen near-neighbours (and one anion) for each cation, whereas there are actually six oxygen near-neighbours: three (for example in sodalite itself) with C-O ~ 2.36 Å and three more with C-O' ~ 3.08 Å (Table I). According to the criteria of Brown and Shannon (1973) both types of C-O distance have significant bond strengths $s(\text{C-O})$ and $s(\text{C-O}')$ which can be calculated from

Table I. Bond distances and angles for aluminosilicate sodalites $C_6(A)_xSi_6O_{24}B_2$ (Estimated standard deviations in parenthesis).

CA sample	LiCl powder	NaCl powder	NaCl single crystal	KCl powder	NaI powder
ACO₃ tetrahedron³:					
C-A _{expt}	2.45 (2)	2.704 (5)	2.730 (3)	3.007 (5)	3.089 (5)
C-A _{calc} ⁴	2.681	2.730	2.730	3.059	3.117
C-O _{expt}	2.09 (2)	2.372 (6)	2.352 (4)	2.747 (12)	2.383 (8)
C-O _{calc} ⁴	2.001	2.351	2.351	2.711	2.351
O-O	3.28 (2)	3.70 (2)	3.690 (7)	4.34 (4)	3.92 (1)
A-O	3.84 (2)	4.30 (2)	4.293 (9)	4.83 (4)	4.45 (1)
ACO	115 (1)	115.8 (5)	115.1 (2)	114.2 (6)	108.1 (3)
LOCO	103 (1)	102.5 (5)	103.3 (2)	104.4 (6)	110.8 (3)
ACO₃ tetrahedron³: (for C-A see above)					
C-O ¹	3.19 (3)	3.083 (9)	3.078 (6)	2.90 (2)	3.01 (1)
O ¹ -O ¹	5.41 (3)	5.23 (2)	5.230 (10)	4.90 (4)	5.18 (1)
A-O ¹	4.40 (2)	4.49 (2)	4.492 (9)	4.62 (4)	4.57 (1)
ACO ¹	102 (1)	101.7 (5)	101.2 (2)	102.9 (6)	97.1 (3)
LOCO ¹	116 (1)	116.0 (5)	116.3 (2)	115.2 (6)	118.5 (3)
SiO₄ tetrahedron⁴:					
Si-O	1.619 (10)	1.592 (8)	1.617 (4)	1.53 (2)	1.668 (6)
2 x O-O	2.679 (14)	2.667 (11)	2.701 (5)	2.55 (2)	2.721 (9)
4 x O-O	2.625 (15)	2.565 (11)	2.609 (5)	2.47 (2)	2.726 (9)
2 x LO ₄ O	111.7 (6)	113.8 (4)	113.3 (2)	113.0 (8)	109.3 (3)
4 x LO ₄ O	108.4 (4)	107.3 (4)	107.6 (2)	107.8 (6)	109.6 (3)
AlO₄ tetrahedron⁴:					
Al-O	1.739 (11)	1.766 (8)	1.740 (8)	1.82 (2)	1.668 (6)
2 x O-O	2.839 (15)	2.909 (11)	2.872 (5)	2.96 (2)	2.721 (9)
4 x O-O	2.840 (14)	2.870 (11)	2.825 (5)	2.97 (2)	as
2 x LO ₄ O	109.4 (4)	111.0 (4)	111.3 (2)	109.2 (7)	above
4 x LO ₄ O	109.5 (5)	108.7 (3)	108.6 (1)	109.6 (6)	r.m.s. dev. (sc) 0.0004
LSiAl	125.6 (4)	138.4 (3)	138.2 (2)	155.4 (9)	145.3 (4)
Si-Al	2.9865 (5)	3.1392 (5)	3.1360 (5)	3.2714 (5)	3.1848 (5)
φ(SiO ₄) ⁵	32.1 (3)	21.8 (3)	22.3 (2)	7.7 (3)	-
φ(AlO ₄)	34.2 (3)	23.9 (3)	25.8 (2)	8.9 (3)	-
φ(mean)	33.1 (2)	22.9 (2)	23.0 (1)	8.3 (2)	19.0 (2)
T-O	1.679 (7)	1.679 (6)	1.678 (3)	1.674 (11)	1.668 (6)
a(C-O) ⁶	0.192	0.199	0.208	0.146	0.193
a(C-O ¹)	0.037	0.046	0.046	0.111	0.052
a(total)	0.229	0.245	0.254	0.257	0.245
R (weighted) ⁷	0.037	0.042	0.077	0.069	0.043
No. of unique reflections	26	25	482	20	23
No. of non-unique reflections	14	20	-	26	16
No. of hkl	60	73	482	85	63

¹ Distances in Å, angles in degrees. 1 Å = 10⁻¹⁰ m.

C⁻ = cavity cation (Li⁺, Na⁺, or K⁺), A⁻ = cavity anion (Cl⁻ or I⁻).

² From Dempsey and Taylor, 1980

³ Each 6-ring has alternating Al-O-Si and Si-O'-Al bridges (see text).

⁴ 2 x and 4 x indicate multiplicities. The former refer to parameters lying within 4-rings, the latter within 6-rings.

⁵ Tilt angles of tetrahedra.

⁶ Bond strengths (see text).

⁷ Crystallographic residual $\sum w|F_o - F_c| / \sum wF_o$.

Table II. Observed and calculated atomic parameters¹ for aluminosilicate sodalites

		$\bar{a} = 8.447(2) \text{ \AA}$			
		$\bar{b} = 8.447(2) \text{ \AA}$			
		$\bar{c} = 8.447(2) \text{ \AA}$			
		$B(O) = 0.57(19), B(Li^+) = 1.2(7), B(Si, Al) = 0.87(6), B(Cl^-) = 1.5(2) \text{ \AA}^2$			
		I	II	III	IV
O	x	0.1424 (14)	0.1393, 0.1382	0.1439	0.1450
	y	0.1311 (13)	0.1313, 0.1301	0.1344	0.1337
	z	0.4108 (7)	0.4106, 0.4058	0.4116	0.4118
Li ⁺	x	0.1675 (24)	0.1842, 0.1770	0.1832	0.1665
r.m.s. dev.		0.0016	0.0085, 0.0058	0.0081	0.0020
		$\bar{a} = 8.879(2) \text{ \AA}$			
		$\bar{b} = 8.879(2) \text{ \AA}$			
		$\bar{c} = 8.879(2) \text{ \AA}$			
		$p: B(O) = 0.80(13), B(Na^+) = 2.30(16), B(Si, Al) = 1.10(6), B(Cl^-) = 2.7(2) \text{ \AA}^2$			
		$sc: B(O) = 0.76(3), B(Na^+) = 1.27(5), B(Si, Al) = 0.43(4), B(Cl^-) = 1.69(5), B(Al) = 0.44(5)$			
		I	II	III	IV ³
O	x(p)	0.1521 (10)	0.1451, -	0.1487	0.1497
	x(sc)	0.1498 (4)	-	-	-
	y(p)	0.1373 (9)	0.1367, -	0.1401	0.1395
	y(sc)	0.1393 (4)	-	-	-
	z(p)	0.4391 (5)	0.4371, -	0.4385	0.4386
	z(sc)	0.4386 (3)	-	-	-
Na ⁺	x(p)	0.1758 (5)	0.1776, -	0.1777	0.1762
	x(sc)	0.1777 (3)	-	-	-
r.m.s. dev. (p)		0.0008	0.0038, -	0.0024	0.0017
r.m.s. dev. (sc)		0.0004	0.0028, -	0.0007	0.0008
		$\bar{a} = 9.253(2) \text{ \AA}$			
		$\bar{b} = 9.253(2) \text{ \AA}$			
		$\bar{c} = 9.253(2) \text{ \AA}$			
		$B(O) = 0.53(26), B(K^+) = 1.7(2), B(Si, Al) = 0.80(9), B(Cl^-) = 2.5(3) \text{ \AA}^2$			
		I	II	III	IV
O	x	0.1586 (17)	0.1496, 0.1502	0.1527	0.1536
	y	0.1363 (18)	0.1410, 0.1414	0.1449	0.1442
	z	0.4786 (12)	0.4715, 0.4786	0.4777	0.4778
K ⁺	x	0.1876 (5)	0.1835, 0.1934	0.1909	0.1891
r.m.s. dev.		0.0014	0.0065, 0.0057	0.0055	corr ¹ 0.0048
		$\bar{a} = 9.008(2) \text{ \AA}$			
		$\bar{b} = 9.008(2) \text{ \AA}$			
		$\bar{c} = 9.008(2) \text{ \AA}$			
		$B(O) = 2.5(2), B(Na^+) = 3.2(3), B(Si, Al) = 2.22(9), B(I^-) = 3.97(11) \text{ \AA}^2$			
		I	II	III	IV: $\bar{a} = 9.008(2) \text{ \AA}$
O	x	0.1428 (7)	0.1467, 0.1468	0.1502	0.1511
	y	0.1428 (7)	0.1382, 0.1383	0.1419	0.1412
	z	0.4508 (7)	0.4467, 0.4479	0.4494	0.4495
Na ⁺	x	0.1980 (6)	0.1980, 0.2001	0.1998	0.1995
r.m.s. dev.		0.0007	0.0021, 0.0035	0.0039	0.0043

¹ Data given for each sodalite: unit cell contents, cell edge a, space group, isotropic temperature factors B, oxygen coordinates (x, y, z), cation coordinate (x, x, x) and root mean square deviations. I: X-ray results. II: Taylor and Henderson, 1978, first set based on T-O = 1.678 Å, second set allows T-O to vary. III: Dempsey and Taylor, 1980. IV: computer modelling, this work. For model data, r.m.s. dev. are calculated from deviations from X-ray values. For X-ray results, r.m.s. dev. are calculated from the experimental e.s.d. given in parenthesis. Other coordinates: A⁻ at (0, 0, 0), Si at (1/2, 0, 1/2), Al at (0, 1/2, 1/2), etc.

² p = powder data; sc = single crystal data.

³ Calculated with a = 8.870 Å.

⁴ Based on estimated C-A distance for K_{7.6}Na_{0.4}(Al₆Si₆O₂₄)Cl₂ (Table III).

the observed C–O lengths (see Table I). The six oxygen neighbours all belong to the same ‘6-ring’ of six Al–O–Si bridges linked in a ring forming one of the hexagonal faces of the basic sodalite framework building unit.

Although the model calculations have the shortcomings described above, they are in fair agreement with experiment with regard to the coordinates of the oxygen atoms (which determine the geometry of the SiO₄ and AlO₄ tetrahedra) except in the case of K_{7.6}Na_{0.4}(Al₆Si₆O₂₄)Cl₂ which has the largest *a* and the most expanded sodalite cage of the samples studied. Despite this, the average Si, Al–O distance *T*–O remains remarkably constant throughout all the sodalites studied (see Table I). Even the 1.668(6) Å for Na₈(Al₆Si₆O₂₄)I₂ is not significantly different from the 1.678 Å regularly adopted in the model calculations. The parameters which measure the degree of structural collapse, the Al–O–Si angle and the tilt angles ϕ , also show good agreement with the model calculations.

Computer modelling. It has already been shown that the use of ionic radii or predetermined C–O distances in earlier models is unsatisfactory. In this section we develop a modelling procedure without any assumptions regarding C–O distances, but using C–A distances calculated from the C–A distances of other materials (see later). Our aim is to calculate atomic coordinates given only the experimental *a* value and a minimum of assumptions. Our treatments of framework geometry and cation coordinates are independent.

(i) Framework geometry. With Si at $\frac{1}{4}$, 0, $\frac{1}{2}$ and Al at 0, $\frac{1}{4}$, $\frac{1}{2}$ the following relationships give the Si–O and Al–O distances *t* and *t'* in terms of the oxygen coordinates *x*, *y*, *z*.

$$t^2/a^2 = (x - \frac{1}{4})^2 + y^2 + (z - \frac{1}{2})^2 \quad (1)$$

$$t'^2/a^2 = x^2 + (y - \frac{1}{4})^2 + (z - \frac{1}{2})^2 \quad (2)$$

Subtraction leads to

$$x - y = 2(t' + t)(t' - t)/a^2 \quad (3)$$

Equations (1)–(3) are *exact*. Following Koch and Hellner (1981), but making the coordinate transformation appropriate to our choice of coordinate system, we note that the following relation holds for sodalites with ideal tetrahedra and ideal oxygen coordinates *x*_i, *x*_i, *z*_i.

$$8(\frac{1}{2} - x_i)^2 - 8(\frac{1}{2} - z_i)^2 = 1 \quad (4)$$

Even in space group *I*43*m*, which requires oxygen coordinates of the form *x*, *x*, *z*, equation (4) is *approximate* because it presupposes exactly tetrahedral O–*T*–O angles. However, the approximation is good for Na₈(Al₆Si₆O₂₄)I₂, in *I*43*m*, because the observed O–*T*–O angles are within 0.2° of the tetrahedral angle (col. 5 in Table I). For sodalites

for which this approximation is valid, solution of equations (4) and (1), with *y*_i = *x*_i, gives a satisfactory value for *x*_i; i.e.

$$x_i = \frac{1}{4} - t_i/3^{\frac{1}{2}}a \quad (5)$$

in our coordinate system, and thence *z*_i from (4). In (5), *t*_i is the mean (and ideal) *T*–O distance. With *t*_i taken as 1.678 Å (see above) good agreement with experiment is obtained for the oxygen coordinates of Na₈(Al₆Si₆O₂₄)I₂; see final column of Table II(*d*). (Agreement is even better with *t*_i = 1.668 Å, the experimental value from Table I.)

We applied (5) and thence (4) to the other sodalites we have studied and found fair agreement of *z*_i with experiment. However, the calculated *x*_i were generally intermediate between the observed *x* and *y* values, usually rather nearer to *y* than *x*. To move towards a treatment applicable in space group *P*43*n*, we shall define *x*_i as a weighted mean of *x* and *y*:

$$x_i = \frac{x + wy}{1 + w} \quad (6)$$

where *w* is a weighting parameter. We shall also take *z*_i to represent the observed *z* coordinate (i.e. *z* = *z*_i). Equation (4) now becomes

$$8[\frac{1}{2} - (x + wy)/(1 + w)]^2 - 8(\frac{1}{2} - z)^2 = 1 \quad (7)$$

in which *w* is an adjustable parameter.

In space group *P*43*n*, the oxygen coordinates *x*, *y*, *z* are the solutions of the non-linear simultaneous equations (1), (3), and (7). We have used a Commodore 4032 microprocessor to solve these equations by an iterative method. The data required for the calculation are the experimental *a* for the sodalite and estimates of the Si–O and Al–O bond lengths *t* and *t'*. After inspection of the experimental values of *t* and *t'*, paying particular attention to the single-crystal results, we chose (for all calculations) to use *t* = 1.618 Å and *t'* = 1.738 Å which maintains *t*_i at 1.678 Å. The calculation of *x*, *y*, and *z* proceeds as follows, and may be carried out for a selection of values of *w*. An initial value of *x* is selected and used to obtain a corresponding value of *y* from (3) and thence a corresponding value of *z* from (7). These *x*, *y*, and *z* values are substituted into the right-hand side of equation (1) and the result compared with *t*²/*a*². Iteration of *x* is then initiated to improve the agreement, and (using successively smaller *x*-increments) an accurate value for *x* is found which, via (3) and (7), satisfies (1).

We have tried a selection of values for the adjustable parameter *w*, and found that reasonable agreement can be obtained between calculated *x*, *y*, and *z* values and the observed values, with *w* = 5 throughout; see the columns labelled IV in Table II.

(ii) Cation coordinates. The cations are situated

at sites of the type x, x, x . If the cation coordinate is denoted as x_c , its relationship with the $C-A$ distance is

$$C-A = 3^{\frac{1}{2}}x_c a \quad (8)$$

Thus x_c may be calculated using the experimental a value and an estimate of the $C-A$ distance. To obtain the latter, the method of Beagley (1975) was employed, in which the estimate is made by interpolation between the experimental values for the $C-A$ distance in gaseous monomeric CA molecules and the $C-A$ distance in the appropriate crystalline alkali halide. The interpolation procedure uses the equations of Brown and Shannon (1973). The bond strength of the $C-A$ bond is $\frac{1}{4}$ in the sodalites, owing to the regular tetrahedral coordination around the A^- ions. The values of x_c obtained by means of (8) are given in Table II (col. IV). The good agreement between the observed and calculated values of x_c , particularly for the Li-sodalite, implies that our estimation of the $C-A$ distance is much more reliable than the estimated $C-O$ distances used in the earlier models.

An attempt has been made in Table II to give a measure of the agreement between model and experiment by calculating the root mean square deviation of the model oxygen and cation coordinates from their observed values. Also given (col. I) is the experimental r.m.s. estimated standard deviation σ for the four observed parameters of each sample. For the four sodalites ($a-d$, Table II) the r.m.s. deviations from experiment of the model coordinates of the present work (col. IV) are respectively about σ , 2σ , 3σ , and 3σ . The best agreement for the earlier models (cols. II and III) are about 4σ , 2σ , 4σ , and 3σ , showing that the

present model is in general slightly better than the earlier ones.

Discussion. The present modelling procedure neither depends on atomic radii nor predetermined $C-O$ distances, but relies instead on $C-A$ distances which are easier to estimate because the $C-A$ bond strength is precisely $\frac{1}{4}$. The present method provides independent calculations for framework coordinates and cation coordinates. Its success demonstrates that the configuration adopted by the aluminosilicate framework is fixed by the a value and a tendency to adopt near ideal SiO_4 and AlO_4 tetrahedra, rather than by the need to adopt precise $C-O$ distances. However, the a distance itself must be fixed by the requirements of the AC_4 tetrahedron. From Table I it can be deduced that the total bond strength around the cations is unity, made up of $s(C-A) = \frac{1}{4}$ and $3[s(C-O) + s(C-O')]$. It is the combined $C-O$ and $C-O'$ strength which is about 2, not the strength of the $C-O$ bond alone.

In Table III, the calculated $C-A$, $C-O$, and $C-O'$ distances of the Dempsey and Taylor (1980) model and the present model are compared with the experimental values. For the chloride sodalites in $P43n$, the estimates of the present model show the better agreement with experiment, in every case. For the potassium-containing sodalite the agreement is further improved when allowance is made for the small amount of sodium also present. In the case of $Na_8(Al_6Si_6O_{24})Cl_2$, in $I43m$, models III and IV reproduce the experimental values equally well; to improve agreement for this sodalite it is necessary to use the shorter $T-O$ distance of 1.668 Å in the calculations.

The poor agreement between model and experimental oxygen coordinates for $K_{7.6}Na_{0.4}(Al_6Si_6$

Table III Cation-anion and cation-oxygen distances (Å) in aluminosilicate sodalites $C_8(Al_6Si_6O_{24})A_2$

CA	C-A			C-O			C-O'	
	expt. ¹	III ²	IV ²	expt.	III	IV	expt.	IV
LiCl	2.45(2)	2.681	2.436	2.09(2)	2.001	2.098	3.19(3)	3.164
NaCl	2.704(5)	2.730	2.707	2.372(6)	2.351	2.362	3.083(9)	3.082
KCl ³	-	3.059	3.032	-	2.711	2.723	-	2.884
$K_{7.6}Na_{0.4}Cl$	3.007(5)	-	3.016 ⁴	2.747(12)	-	2.729	2.90(2)	2.888
NaI	3.089(5)	3.117	3.113	2.383(8)	2.351	2.342	3.01(1)	3.040

1 Powder studies.

2 Calculated distances. III: Dempsey and Taylor, 1980. IV: this work.

3 Based on a for $K_{7.6}Na_{0.4}(Al_6Si_6O_{24})Cl_2$.

4 $(7.6 \text{ K-Cl} + 0.4 \text{ Na-Cl})/8$. For corresponding corrected x_c , see Table II.

$O_{24})Cl_2$ persists and appears to manifest itself in distortion of the SiO_4 and AlO_4 tetrahedra which the present model cannot reproduce; all other experimental parameters agree well with the values obtained in the model calculations. It is unfortunate that of the X-ray films studied, those for this sodalite had the poorest quality. This is reflected in the higher residual, R , and the much higher errors for the oxygen coordinates, but not in the error in the x -coordinates of the heavy potassium atom. It is believed that this lower quality and precision is reflected in the poorer agreement between the observed framework geometry and that predicted by the model. This sodalite is of special interest because of its large a value of 9.253 Å. It has the most expanded sodalite cage of those studied [ϕ (mean) = 8.3° and $\angle Si-O-Al = 155.4^\circ$ (Table I)] and thus the largest z -coordinate, 0.4786. It therefore belongs to the Dirichlet domain type 2.2 (Koch and Hellner, 1981) whereas the other, more collapsed, sodalites studied belong to type 2.3 because their z -coordinates are less than the limiting value of 0.4613. The potassium-containing sodalite contrasts further with the others in the behaviour of its $C-O$ and $C-O'$ distances; the latter differ by only about 0.15 Å which corresponds to a strength difference of only 0.035 (Table I). In the other sodalites studied, the strength differences between the $C-O$ and $C-O'$ distances are all $c. 0.15$. (As noted above, however, the total strength is $c. \frac{1}{4}$ in all cases.)

Although at the outset of the present study one of the main concerns was to establish a relationship between $T-O$ distances and $T-O-T$ angles, the X-ray results, coupled with the computer modelling, suggest that the $T-O$ distance t_i remains little changed at 1.678 Å throughout the sodalites examined, except perhaps that 1.668 Å is a better estimate in the $I\bar{4}3m$ case. The structural refinement of $Na_8(Al_6Si_6O_{24})I_2$ in $I\bar{4}3m$ implies disordered Si and Al sites, which seems unlikely when other sodalites, with closely similar chemistry, have ordered arrangements ($P\bar{4}3n$). However, a similar situation appears to exist regarding the structure of nosean (Schulz and Saalfeld, 1965) in relation to haüyne (Löhn and Schulz, 1968). The much higher isotropic temperature factors of all the atoms in $Na_8(Al_6Si_6O_{24})I_2$ suggest a form of positional disorder, possibly as a result of superstructure. Unfortunately, this aspect of the work

cannot be taken further by the experimental techniques used here. In this context it should be noted that most of the aluminate-sodalites are not cubic despite their simple chemical compositions (Depmeier, 1979; Henderson and Taylor, 1979b). It seems likely, therefore, that the structure determined for $Na_8(Al_6Si_6O_{24})I_2$ is the 'averaged' structure of the 9 Å cubic pseudocell.

The results clearly show that, as expected, the tilt angle, ϕ , decreases and the $T-O-T$ angle increases as the cavity ions increase in size and that the $T-O-T$ angle is the dominant structural variable of the sodalite framework in relation to compositional, and perhaps thermal, expansion.

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