conduction plane is unable to expand infinitely because the spinel blocks interleaving the plane are joined with the Ga(3)—O(5)—Ga(3) bond. In order to relax the steric repulsion between K$^+$ and O(4), the Ga(3)—O(5)—Ga(3) bond, which is kinked in sodium β''-gallate, becomes straight and the O(4) atom recedes from the K$^+$ ion. On the other hand, in sodium β''-gallate, the conduction plane is thick enough for Na$^+$ and hence the O(4) atom is allowed to keep moderate distances from Ga(1) and O(1).

The TO layer (Fig. 2c, No. 3) is placed in the midst of the spinel block and furthest from the conduction planes. Ga(4) is coordinated with six O(1) atoms. This octahedron exhibits hardly any deformation owing to different cations in the conduction plane. The mismatches observed between sodium and potassium β''-gallate are within 0·001 Å in the Ga(4)—O(1) distance, and within 0·3° in the O(1)—Ga(4)—O(1) bonding angle. However, the Ga(2)O$_4$ tetrahedron exhibits distinct changes between the two salts, although it would be little influenced by the conduction planes. Na atoms are introduced into the Ga(2) site in sodium β''-gallate. Potassium β''-gallate, obtained by cation exchange from sodium β''-gallate, also contains Na atoms at the Ga(2) site in the spinel blocks. The occupancies of Na at the Ga(2) site in sodium and potassium β''-gallate, 16·3 and 8·7%, reflect the mean Ga(2)—O distances in the gallates, 1·911 and 1·902 Å, respectively. The expansion of Ga(2)O$_4$ tetrahedra in sodium β''-gallate is mainly caused by the shift of O(3) atoms. Ga(2)—O(1) is only 0·006 Å longer in sodium β''-gallate than in potassium β''-gallate, while Ga(2)—O(3) is 0·018 Å longer. O(1)—O(1) distances in both sodium and potassium β''-gallate are almost the same, while the former has O(1)—O(3) distances clearly larger than the latter.

Therefore, the Ga(2)O$_4$ tetrahedron in sodium β''-gallate is mainly expanded in the direction of the c axis.

The effect of cation substitution in β''-gallates appears most prominently in the dimension of the c axis, which has been roughly explained by the variation in the thickness of the conduction planes. Furthermore, Tsurumi et al. (1987) noted that some differences in coordination polyhedra are observed between the spinel blocks of potassium and ammonium β''-gallate. The present study has shown that the deformation of coordination polyhedra in the spinel block is caused by the substitution of Na for K, differing from the situation observed between potassium and ammonium β''-gallate.

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Orientational Disorder of the Nitrite Anion in the Sodalite Na$_8$[AlSiO$_4$]$_6$(NO$_2$)$_2$

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Abstract. $M_r = 990·30$, cubic, $P\bar{4}3n$, $a = 8·923\,(1)$ Å, $V = 710·45$ Å^3, $Z = 1$, $D_m = 2·35$, $D_x = 2·31$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0·71073$ Å, $\mu = 0·70$ mm^{-1}, $F(000) = 488$, room temperature, $R = 0·021$ for 304 unique observed reflections. The sodalite framework is an ordered and alternating array of corner-sharing AlO$_4$

and SiO_4 tetrahedra. Each polyhedral $[4^66^8]$ cage contains four Na cations which surround tetrahedrally an NO_2 anion. The N atom is placed about 0.37 Å away from the centre of the cage. The orientational disorder of the anion is at least twelvefold, and strong interactions of its N and O atoms with Na cations exist.

Introduction. Nitrite sodalites of various chemical compositions have been recently synthesized and characterized by means of X-ray powder diffraction, thermoanalysis, IR and MAS NMR spectroscopy; intracage oxidation of nitrite to nitrate has been observed at elevated temperatures (Hund, 1984; Weller & Wong, 1988; Buhl, Gurris & Hoffmann, 1989a,b; Kempa, Engelhardt, Buhl, Felsche, Harvey & Baerlocher, 1990; Weller, Wong, Adamson, Dodd & Roe, 1990; Buhl, Sieger, Engelhardt & Felsche, 1990). The crystal structure has been determined at room temperature by an X-ray powder Rietveld analysis (Kempa et al., 1990), and by an X-ray single-crystal study (Buhl, Löns & Hoffmann, 1989). In both cases the samples did not possess the ideal chemical composition $Na_8[AlSiO_4]_6(NO_2)_2$, and stoichiometries of $Na_8[AlSiO_4]_6(NO_2)_{2-x}(OH.H_2O)_x$ with $x = 0.15$ and $Na_8[AlSiO_4]_6(NO_2)_2.1.4H_2O$ have been stated, respectively. Both analyses showed the structure to be cubic with space group $P\bar{4}3n$, and the sodalite framework to be an ordered array of corner-sharing AlO_4 and SiO_4 tetrahedra, in agreement with ^{29}Si MAS NMR spectroscopic data (Kempa et al., 1990). However, different positions for the non-framework constituents Na^+ and NO_2^-, which are imbibed in the $[4^66^8]$ sodalite cages, have been reported. In addition, the reliability of the given models of disorder is affected by the non-stoichiometric composition of the samples. Since we have now been able to synthesize large single crystals of good quality, we have carried out an additional X-ray single-crystal structure analysis. The results are reported here.

Experimental. Crystals synthesized hydrothermally. Typical reaction mixture: 0.8 mmol calcined (1800 K, 2 h) kaolinite, 4 mmol $NaNO_2$ and 2 ml $8M$ NaOH; kept in Ag ampoules for seven days at $\sim$ 100 MPa and 620 K (temperature at the bottom of the autoclave, vertical temperature gradient 3 K cm^{-1}). Product washed with deionized water, dried at 370 K, and analysed by means of X-ray powder diffraction, simultaneouos thermoanalysis, IR and MAS NMR spectroscopy as described elsewhere (Kempa et al., 1990; Buhl, Sieger, Engelhardt & Felsche, 1990); no NO_3^-, OH^- and/or H_2O detected within the limits of accuracy ($< 5\%$). Rhombic dodecahedral crystal 0.3 × 0.3 × 0.1 mm, D_m by pycnometry, precession photographs showed sharp

reflections. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, lattice constants from 25 reflections, $16.9 < \theta < 17.1°$, variable $\omega/2\theta$-scan technique, 3049 intensities measured up to $(\sin\theta)/\lambda = 0.995$ Å^{-1} in the hemisphere $0 \le h,k,l \le 17$, crystal alignment and stability monitored by three standard reflections, no corrections for absorption, 558 unique reflections after merging equivalent ones ($R_{int} = 0.073$), 254 reflections with $I < 2.0\sigma(I)$ considered unobserved and excluded from structure refinement.

First coordinates for the framework atoms Al, Si, O1, and the non-framework cation Na taken from the X-ray powder refinement (Kempa et al., 1990), full-matrix least-squares method, function minimized $\sum w(\Delta F)^2$, 304 observed reflections weighted according to $w = 4F^2/[\sigma^2(I) + (0.04F^2)^2]$. Positions of atoms N and O2 (belonging to the NO_2 anion) from difference Fourier synthesis on site $2(a)$ (0,0,0; centre of the cage) and on site $24(i)$ (x,y,z), respectively. After refinement ($R = 0.022$, $wR = 0.031$) a large isotropic displacement parameter $[U = 0.109 (6)$ Å$^2]$ of the N atom as well as the residual electron densities in ΔF map on site $2(a)$ ($\Delta\rho_{min} = -0.59$ e Å^{-3}) and on site $8(e)$ (x,x,x) with $x = 0.03$ ($\Delta\rho_{max} = +0.57$ e Å^{-3}) indicated an off-centre position for the N atom. Refined occupancy factors of atoms Na, N, and O2 not significantly different from values expected for $Na_8[AlSiO_4]_6(NO_2)_2$. Some models of orientational disorder of the anion with N in off-centre position tested by refinement employing no constraints, and assigning isotropic and anisotropic displacement parameters to the atoms of the anion and all other atoms, respectively; two of the models are considered further: model I of twelvefold disorder with N on site $8(e)$ (statistical occupancy factor: s.o.f. = 3/12) and O2 on site $24(i)$ (s.o.f. = 2/12), and model II of sixfold disorder with N on site $12(f)$ (s.o.f. = 1/6) and O2 on site $24(i)$ (s.o.f. = 1/6). For both models: 24 parameters varied, extinction parameter refined to $g = 0.0000030$ (1), Δ/σ in last cycle 0.0. Model I: $R = 0.021$, $wR = 0.030$, $S = 0.725$; ΔF map showed $\Delta\rho_{max} = +0.57$ e Å^{-3} (at 0.14,0,0) and $\Delta\rho_{min} = -0.44$ e Å^{-3} (at 0.33,0.33,0.33). Model II: $R = 0.022$, $wR = 0.030$, $S = 0.765$; ΔF map showed $\Delta\rho_{max} = +0.61$ e Å^{-3} (0.14,0,0) and $\Delta\rho_{min} = -0.45$ e Å^{-3} (0,0,0). Final atomic parameters are listed in Table 1;* with the exception of the N atom respective atomic parameters of the two models do not differ by more than their e.s.d.'s. Only minor differences between $|F_c|$ for the two models, indicating the insensitivity of X-ray diffraction for localiz-

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* Lists of structure factor amplitudes and anisotropic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53509 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates and equivalent isotropic displacement parameters* ($Å^2$) *with e.s.d.'s in parentheses for model* I

$$U_{eq} = (1/24\pi^2)\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	Site	Occupancy	x	y	z	U_{eq}
Si	6(c)	1	$\frac{1}{4}$	$\frac{1}{4}$	0	0·0076 (1)
Al	6(d)	1	$\frac{1}{4}$	0	$\frac{1}{2}$	0·0070 (1)
O1	24(i)	1	0·14008 (8)	0·15032 (9)	0·4428 (1)	0·0127 (1)
Na	8(e)	1	0·1854 (1)	x	x	0·0240 (1)
O2	24(i)	$\frac{1}{6}$	0·045 (2)	−0·1055 (9)	0·040 (2)	0·079 (6)
N,I	8(e)	$\frac{1}{4}$	0·025 (1)	x	x	0·046 (5)
N,II	12(f)	$\frac{1}{6}$	0·040 (2)	0	0	0·052 (6)

For model II there are no significant differences with the exception of N.

ing the highly disordered low-scattering atoms more accurately, and for distinguishing significantly between the two models considered, although model I seems to provide a somewhat better fit to experimental data.

Complex scattering factors for neutral atoms and the Na cation taken from *International Tables for X-ray Crystallography* (1974, Vol. IV), all computations carried out on a Digital VAX3200 work station using the Enraf–Nonius (1989) *SDP* program system, illustrations generated with the program *ORTEP*II (Johnson, 1976).

Discussion. This single-crystal study confirms excellently the results of the recent X-ray powder Rietveld refinement of nitrite sodalite as far as the fractional coordinates of the framework atoms and the O atoms (O2) of the NO_2 anion are concerned (Kempa *et al.*, 1990). However, along with generally higher accuracy, a more detailed account of the orientational disorder of the anion in the centre of each [4^66^8] sodalite cage has been reached. For a discussion of the 3-dimensional 4-connected sodalite TO_2 framework, and an illustration of one cage with the four non-framework Na cations, which are located close to six-membered rings of the framework, and the twelve O2 atomic positions of the disordered anion see Kempa *et al.* (1990), Fig. 2. Two models of anionic disorder are considered here, one of the possible NO_2^- orientations in each model is shown in Fig. 1. Selected interatomic distances and angles are summarized in Table 2.

Refinements and difference Fourier syntheses clearly revealed that the N atom of the NO_2 anion is not located at the centre of the cage [site 2(a), point symmetry 23], as is to be expected for this anion with point symmetry *mm*2 and with the centre of gravity 0·48 Å away from the N atom. This was already inferred from the results of the Rietveld refinement (Kempa *et al.*, 1990), and is in contrast to the recent single-crystal study (Buhl, Löns & Hoffmann, 1989). The orientational disorder of the anion with the N atom in off-centre position can be approximated by

two borderline models, the true N positions being somewhere in between. In both models the N atom is shifted by *ca* 0·37 Å away from the centre of the cage, in model I along the threefold axes [site 8(e)] of the structure in the directions to − not away from − the Na cations, and in model II along the twofold axes [site 12(f)] of the structure. The disorder is twelvefold in the case of model I with statistical occupancy factors (s.o.f.'s) of 3/12 for the N atom and 2/12 for the O2 atom, respectively, *i.e.* the N position given in Table 1 is the average of three close positions and the O2 position given in Table 1 is the average of two close positions. In the case of model II the disorder may be interpreted as sixfold or twelvefold with s.o.f.'s of 1/6 or 2/12 for the atoms N and O2, respectively. The two models differ only in the coordinates of the N atom [*i.e.* N,I···N,II = 0·34 (4) Å], all other respective atomic coordinates being equal within their e.s.d.'s. The true disorder should be regarded at least twelvefold.

Keeping the limited accuracy in mind, both models give reasonable geometric parameters for the NO_2 anion (see Fig. 1 and Table 2), when compared with dimorphic $NaNO_2$: N—O = 1·240 Å and O—N—O = 114·9° at room temperature (Kay, 1972; Kay, Gonzalo & Maglic, 1975). The Na cations are bonded to three O1 framework atoms [Na···O1 = 2·353 (1) Å], and, in addition, to O2 atoms [Na···O2 between 2·47 (5) and 2·54 (5) Å] and/or N atoms [Na···N between 2·48 (1) and 2·67 (1) Å] of the anion. The following coordinations are observed: 3 × O1 + 1 × O2 for two Na, 3 × O1 + 2 × O2 for one Na, and 3 × O1 + 1 × N for one Na in model I; and 3 × O1 + 1 × O2 for two Na, and 3 × O1 + 1 × O2 + 1 × N for two Na in model II. Due to disorder and the borderline character of the models discussed, the stated interatomic distances do not represent true, but only averaged internuclear separations. These averaged bond lengths are in reasonable agreement with respective ones found in $NaNO_2$: Na···O = 2·471 and 2·553 Å, and Na···N = 2·589 Å at room temperature (Kay, 1972).
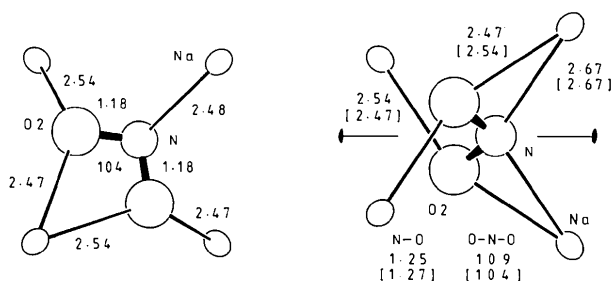

Fig. 1. One of the possible orientations of the disordered NO_2 anion with the four Na cations in model I (left), and model II (right). Bond lengths in Å, and bond angles in degrees. In model II the disorder gives reasonable geometries for the anion in two ways.

Table 2. *Selected interatomic distances* (Å) *and angles*
(°) *with e.s.d.'s in parentheses*

Framework, model I*

Si—O1	1·6167 (9)	Al—O1	1·7383 (9)
O1—Si—O1 (2×)	113·2 (1)	O1—Al—O1 (2×)	111·3 (1)
O1—Si—O1 (4×)	107·6 (1)	O1—Al—O1 (4×)	108·6 (1)
Si—O1—Al	140·2 (1)		

Na coordination, model I

Na⋯O1	2·353 (2)	Na⋯O1	3·043 (2)
Na⋯O2	2·47 (5)	Na⋯O2	2·54 (5)
Na⋯O2	3·16 (3)	Na⋯N	2·48 (1)
Na⋯N	3·01 (1)		

Na coordination, model II

Na⋯O1	2·353 (2)	Na⋯O1	3·043 (2)
Na⋯O2	2·47 (5)	Na⋯O2	2·54 (5)
Na⋯O2	3·14 (3)	Na⋯N	2·67 (1)
Na⋯N	3·09 (2)		

NO₂ anion, model I

N—O2 (2×)	1·18 (3)	O2—N—O2	104 (2)
O2⋯O1	3·54 (3)	N⋯O1	4·03 (1)

NO₂ anion, model II

N—O2 (2×)	1·25 (3)	O2—N—O2	109 (5)
or			
N—O2 (2×)	1·27 (3)	O2—N—O2	104 (5)
O2⋯O1	3·54 (3)	N⋯O1	4·03 (3)

* For model II no significant differences.

Strong Na⋯N interactions, which clearly exist in the structure, have not been found in the earlier structure analyses. These interactions are also required from valence bond considerations. The Na environments discussed recently (Kempa *et al.*, 1990) with one cation being fivefold, two cations being fourfold, and one cation being threefold bonded to O2 and/or O1 atoms are very unlikely, because of the highly inhomogeneous coordinations and unbalanced valences. These are, and can obviously only be,

avoided with the N atom in off-centre position. No strong interactions occur between atoms of the anion and O1 framework atoms: N⋯O1 ≥ 4·03 (1) Å, and O2⋯O1 ≥ 3·54 (4) Å.

At room temperature the orientational disorder has to be regarded as dynamic in nature, at least on the NMR time scale. This is shown by the single quadrupolar ^{23}Na MAS NMR signal, which reveals that on average in time only one kind of Na coordination exists in the structure (Kempa *et al.*, 1990).

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Structure of K₃Na[Re₂O₃(CN)₈].2H₂O

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Abstract. Potassium sodium μ-oxo-bis[oxotetra-cyanorhenium(V)] dihydrate, $M_r = 804·9$, ortho-rhombic, *Fmmm*, $a = 8·207$ (2), $b = 13·715$ (5), $c = 16·199$ (7) Å, $V = 1823$ (1) Å³, $Z = 4$, $D_x = 2·932$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 14·2$ mm⁻¹, $F(000) = 1464$, $T = 295 \pm 1$ K, $R = 0·035$

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