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Structure of a High-Silica Variety of Zeolite Na-P

By Ulf Håkansson and Lars Fälth

Munters Zeol AB, Kalkstensvägen 1, *S*-223 78 *Lund, Sweden*

and Staffan Hansen*

Inorganic Chemistry 2, *Chemical Center, University of Lund, PO Box* 124, *S*-221 00 *Lund, Sweden*

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Abstract. $Na_{3\cdot6}Al_{3\cdot6}Si_{12\cdot4}O_{32}.14H_2O$, $M_r = 1292\cdot4$, tetragonal, $I4_1/amd$, $a = 9\cdot9989$ (4), $c = 10\cdot0697$ (4) Å, $V = 1006\cdot75$ (7) Å^3, $Z = 1$, $D_x = 2\cdot13$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6\cdot57$ cm^{-1}, $F(000) = 656$, room temperature, $R = 0\cdot037$ for 1119 unique reflections with $I > 3\sigma(I)$. A single-crystal fragment, cut from an aggregate of twinned crystals, was used for the structure analysis. The tetrahedral framework in this structure represents the highest possible symmetry of a gismondine type of network. The framework is similar to that in the Na-P1 variety of the zeolite, *e.g.* both exhibit body-centred symmetry and pseudo-cubic lattice dimensions, though the silica content is higher in the present structure. The JCPDS Powder Diffraction File No. for $Na_{3\cdot6}Al_{3\cdot6}Si_{12\cdot4}O_{32}.14H_2O$ is 40–1464.

Introduction. Tetrahedral frameworks with the gismondine topology are found in several chemical systems and since this type of framework is non-rigid it adopts various conformations depending on the composition (see references cited by Meier & Olson, 1987). The gismondine-related phases occurring in hydrothermal sodium–aluminosilicate systems are called P zeolites. This single-crystal X-ray investigation of a P zeolite, which is silicon rich compared with other P varieties, was undertaken since most work concerning P zeolites has been performed using powder diffraction techniques, where the special lattice geometry of P phases causes problems due to peak overlap.

Experimental. Analcime and spherulitic crystal aggregates of Na-P, with diameters of up to 1 mm, were synthesized in a steel autoclave by reaction of 2 g of glass, composition $2Na_2O.Al_2O_3.8SiO_2$, and 10 ml, 0·1 mol l^{-1} NaOH(aq.), at 473 K for a period of 7 d (Fälth, 1981). Complex twin crystals of Na-P were also observed and the ideal shape of these twins can be described as a rounded octahedron with concave faces. A large number of crystal aggregates were dissected using a razor blade, in order to locate a crystal fragment exhibiting single-crystal diffraction characteristics. The selected triangular prism had a length of 0·42 mm and the sides were approximately 0·17 × 0·12 × 0·12 mm wide. D_m was not determined since the sample consisted of two phases. Data were collected using a Nicolet $P3m$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scan width $\Delta 2\theta = 2\cdot4° + \alpha_1\alpha_2$ splitting, scan rate 1·0–29·3° min^{-1}, total background time = 0·75 × scan time. Cell parameters were determined from 38 single-indexed lines from a Guinier–Hägg pattern, λ(Cu $K\alpha_1$) = 1·54056 Å, recorded with a sample consisting of ground twin crystals, hand picked under the light microscope, from the preparation producing the single-crystal fragment. The diffraction symmetry and systematic absences observed on Weissenberg films and in preliminary diffractometer runs indicated the crystal symmetry to be $I4_1/amd$. A data set with $[(\sin\theta)/\lambda]_{\max} = 1\cdot18$ Å^{-1}, h, k and l all 0 to 23, 3802 reflections, was collected. Averaging of hkl and khl, $R_{\rm int} = 0\cdot038$, resulted in 1119 unique reflections with $I > 3\sigma(I)$. Standard reflections 600 and 112 were monitored after every 100 reflections and showed a random variation in intensity. Lp corrections were performed, while no absorption correction was applied, since the linear absorption coefficient is low. Tetrahedral framework positions of a gismondine type of net were used for the initial phasing and the structure was then completed by Fourier methods and least-squares refinement minimizing $\sum w(\Delta F)^2$, with $w^{-1} = \sigma^2(F_o) + (0\cdot030F_o)^2 + 0\cdot25$.

Energy dispersive X-ray analysis undertaken with a Philips EM400 transmission electron microscope indicated an Si/Al peak area ratio of 3·47 (9), based on 15 analyses. This suggested an average of 3·6 Al atoms per unit cell and the occupancy factor of Na$^+$ was fixed accordingly in the refinements. The population of the water-molecule sites was assigned in proportion to their relative peak heights in the difference maps. When the occupancy factors of the water molecules were released, insignificant changes in the populations were observed, coupled with large

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* To whom all correspondence should be addressed.

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Table 1. *Positions, displacements and occupancy factors*

The number of atoms per unit cell is 32*g*. *T* represents Si and Al, while *W* designates O atoms in water molecules.

$$B_{eq} = 4/3(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

	x	*y*	*z*	B_{eq}(Å^2)	*g*
T(1)	0·15562 (2)	0·59439 (2)	0·125	0·969 (5)	0·5
O(1)	0	0·5693 (1)	0·1681 (1)	2·21 (2)	0·5
O(2)	0·25	0·5518 (2)	0·25	2·61 (2)	0·5
Na(1)	0·065 (2)	0·404 (2)	0·358 (1)	8·7 (6)	0·1111
W(1)	0	0·506 (8)	0·538 (2)	10 (1)	0·1111
W(2)	−0·143 (3)	0·25	0·254 (5)	11 (1)	0·1111
W(3)	0	0·25	0·535 (2)	13 (2)	0·0555
W(4)	−0·106 (6)	0·25	0·393 (7)	12 (2)	0·0555

Table 2. *Selected distances* (Å)

Tetrahedron

T(1)—O(2)	1·6299 (4)
T(1)—O(2^{i})	1·6299 (4)
T(1)—O(1)	1·6348 (5)
T(1)—O(1^{ii})	1·6348 (5)
Mean	1·6324

Na$^+$ coordination (including Na—O distances in the range 2·4–3·3 Å)

Na(1)—*W*(3)	2·45 (2)	Na(1)—*W*(4^{v})	2·68 (6)
Na(1)—*W*(1^{iii})	2·46 (7)	Na(1)—*W*(2)	2·79 (4)
Na(1)—*W*(2^{iv})	2·59 (5)	Na(1)—*W*(1^{vi})	2·86 (7)
Na(1)—O(2)	2·60 (1)	Na(1)—O(2^{vii})	2·93 (2)
Na(1)—O(1)	2·61 (2)		

Symmetry code: (i) $\frac{3}{4}-y, \frac{1}{4}+x, z-\frac{1}{4}$; (ii) $\frac{3}{4}-y, \frac{3}{4}+x, \frac{1}{4}-z$; (iii) $\frac{3}{4}-y, \frac{1}{4}-x, z-\frac{1}{4}$; (iv) $\frac{1}{4}-y, \frac{3}{4}+x, \frac{1}{4}+z$; (v) $y-\frac{1}{4}, \frac{1}{4}+x, \frac{3}{4}-z$; (vi) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (vii) $y-\frac{1}{4}, \frac{3}{4}-x, \frac{1}{4}+z$.

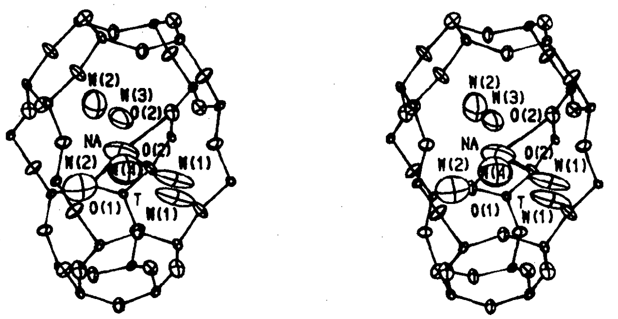

Fig. 1. Coordination of an Na$^+$ ion seen approximately along **b**; the *c* axis is vertical. All water molecules within a distance of 2·4 to 3·3 Å have been included.

correlations between occupancy factors and temperature coefficients. Consequently, the occupancy factors were reset to their original values and were kept fixed in all subsequent calculations. The final cycle of refinement, $(\Delta/\sigma)_{max} = 0{\cdot}69$, resulted in $R = 0{\cdot}037$, $wR = 0{\cdot}051$, $S = 0{\cdot}96$, when 48 parameters, including anisotropic temperature coefficients for all atoms, were varied. The final difference map was featureless, $\Delta\rho_{max} = 0{\cdot}6$, $\Delta\rho_{min} = -0{\cdot}4$ e Å^{-3}. Scattering factors for neutral atoms, including dispersion terms, were taken from *International Tables for X-ray Crystallography* (1974). The form factor of Si was utilized for the atom at the center of the tetrahedron. All computer programs used in the calculations have been listed by Lundgren (1982). Atomic parameters are listed in Table 1 and selected distances in Table 2.* A view of an Na$^+$ ion and its surroundings is presented in Fig. 1.

Discussion. The gismondine type of net has here been refined in its highest possible symmetry. Zeolites with the gismondine framework are known to adopt symmetries ranging from tetragonal to monoclinic (see references cited by Meier & Olson, 1987). An independent test of the framework composition is offered by the average (Si,Al)—O distance and using the same interpolation procedure as in the discussion of the crystal structure of Na-P2 (Hansen, Håkansson & Fälth, 1990), the Al content of the tetrahedron is estimated to be 17%. This corresponds to 2·8 Al atoms per unit cell, which is in reasonable agreement with the chemical analysis.

The positions of the Na$^+$ ion and water molecules *W*(1)–*W*(3) relative to the framework are similar to those observed in Na-P2, when the difference in symmetry is neglected.

The present structure and the Na-P1 structure of Baerlocher & Meier (1972) both exhibit body-centered tetragonal symmetry and pseudo-cubic lattice geometry, but the compositions differ significantly, since a unit-cell content of $Na_6Al_6Si_{10}O_{32}.12H_2O$ was adopted for Na-P1. The silicon content of the structure presented here is also slightly higher than that of Na-P2.

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* Lists of structure factors, anisotropic vibration coefficients and powder diffraction data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52809 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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