Acta Cryst. (1990). **C46**, 1361–1362

Structure of Synthetic Zeolite Na-P2

By Staffan Hansen*

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

and Ulf Håkansson and Lars Fälth

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

(*Received* 19 *September* 1989; *accepted* 19 *November* 1989)

Abstract. $Na_4Al_4Si_{12}O_{32}.14H_2O$, $M_r = 1301{\cdot}1$, orthorhombic, *Pnma*, $a = 9{\cdot}868$ (2), $b = 10{\cdot}082$ (2), $c = 10{\cdot}098$ (2) Å, $V = 1004{\cdot}6$ (3) Å^3, $Z = 1$, $D_x = 2{\cdot}15$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 6{\cdot}61$ cm^{-1}, $F(000) = 660$, room temperature, $R = 0{\cdot}053$ for 1462 independent reflections with $I > 3\sigma(I)$. An untwinned crystal fragment was located for the structure determination. The tetrahedral framework of Na-P2 represents a new conformation of the flexible gismondine type of net (maximum symmetry $I4_1/amd$). The two almost identical cell constants in Na-P2 do *not* correspond to the topologically tetragonal axes of the gismondine framework.

Introduction. P zeolites are among the many phases which can be produced in the technically important system Na_2O–Al_2O_3–SiO_2–H_2O. Structural characterization of P phases has been complicated by (i) the existence of several topologically distinct zeolite nets with related unit-cell dimensions (gismondine–phillipsite–merlinoite), (ii) the small crystal size, which hinders or prevents single-crystal work and causes broad powder diffraction peaks, and (iii) the strong pseudo-symmetry, which leads to complex twinning and peak overlap in powder patterns. The present single-crystal study was undertaken in order to resolve some of the structural problems concerning P zeolites.

Experimental. Needle-shaped multiply twinned crystals forming spherical aggregates with an approximate diameter of 0·5 mm were produced by the reaction of aqueous NaOH and sodium aluminosilicate glass at 423 K (Fälth, 1981). Around ten twinned crystals were cut with a razor blade and their X-ray diffraction symmetry was checked using both a Weissenberg camera and a diffractometer. The selected crystal fragment exhibited maximum deviation from tetragonal symmetry. It was a triangular prism, length 0·16 mm, sides 0·11, 0·09, 0·07 mm. Data were collected using a Nicolet *P*3*m* diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, ω–2θ scan, width $\Delta 2\theta = 2{\cdot}4° + \alpha_1\alpha_2$ splitting, scan rate 1·0–15° min^{-1}, total background time = 0·75 × scan time. Cell parameters were determined from 12 reflections, λ(Cu $K\alpha$) = 1·54178 Å, $6 < \theta < 28°$, plus 10 reflections, λ(Mo $K\alpha$) = 0·71069 Å, $3 < \theta < 12°$. The data set has $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}91$ Å^{-1}; h 0 to 17; k and l 0 to 18. 3542 unique reflections were measured, of which 1462 have $I > 3\sigma(I)$. The standard reflection $1\bar{1}2$ was monitored after every 100 reflections and showed a random variation in intensity with $\sigma = 2{\cdot}1\%$. Lp and absorption corrections were applied, the range of transmission factors was 0·95–0·98. The Na-P2 structure was initially solved and refined in the space group $P2_12_12_1$, though the symmetry was later increased to *Pnma* ($P2_12_12_1$ is a subgroup of *Pnma*). Tetrahedral nodes (Si,Al) were located by direct methods (*MULTAN*) and the structure was completed by Fourier methods and least-squares refinement minimizing $\sum w(\Delta F)^2$, with $w^{-1} = \sigma^2(F_o) + (0{\cdot}025\,F_o)^2 + 0{\cdot}8$. The final cycles of refinement converged to $R = 0{\cdot}053$, $wR = 0{\cdot}067$, $S = 1{\cdot}18$. Anisotropic temperature factors were used for all atoms; in total 106 parameters were varied, $(\Delta/\sigma)_{\max} = 0{\cdot}03$; $\Delta\rho_{\max} = 0{\cdot}6$, $\Delta\rho_{\min} = -0{\cdot}5$ e Å^{-3}. Scattering factors for neutral atoms, including dispersion terms, were taken from *International Tables for X-ray Crystallography* (1974). For computer programs used, see Lundgren (1982). Atomic parameters are listed in Table 1 and selected distances in Table 2.† Fig. 1 gives a view of the species surrounding an Na^+ ion in the zeolite cage.

Discussion. The topology of the Na-P2 tetrahedral framework is of the gismondine type. This type of 3D net is found in at least four minerals: amicite, garronite, gismondine, gobbinsite, as well as in

---

* To whom all correspondence should be addressed.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52782 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/90/081361-02$03.00

Table 1. *Positions, displacements and occupancy factors*

The number of atoms per unit cell is 8*g*. *T* represents Si,Al; *W* represents O atoms of water molecules. $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	*y*	*z*	B_{eq}(Å^2)	*g*
T(1)	0·35946 (9)	0·0946 (1)	0·35738 (9)	0·91 (1)	1
T(2)	0·17412 (9)	0·0946 (1)	0·10142 (9)	0·92 (1)	1
O(1)	0·2916 (3)	−0·0005 (3)	0·4723 (3)	1·96 (5)	1
O(2)	0·3318 (5)	0·25	0·3999 (4)	2·01 (7)	0·5
O(3)	0·1861 (5)	0·25	0·0530 (4)	1·99 (7)	0·5
O(4)	0·0225 (3)	0·0621 (3)	0·1615 (3)	1·80 (5)	1
O(5)	0·2869 (3)	0·0593 (3)	0·2153 (3)	2·16 (5)	1
Na(1)	0·045 (1)	−0·0808 (7)	0·3520 (7)	8·1 (2)	0·5
W(1)	0·200 (3)	0·75	0·286 (2)	8·5 (6)	0·25
W(2)	−0·031 (2)	0·75	0·529 (2)	14 (1)	0·25
W(3)	−0·006 (1)	0·054 (2)	0·539 (1)	10·2 (6)	0·5
W(4)	−0·132 (3)	0·75	0·411 (2)	9·3 (6)	0·25
W(5)	0·115 (5)	0·75	0·203 (2)	13 (1)	0·25
W(6)	−0·107 (4)	0·75	0·235 (3)	13 (1)	0·25

Table 2. *Selected distances* (Å)

Tetrahedra			
T(1)—O(5)	1·642 (3)	*T*(2)—O(5)	1·639 (3)
—O(1)	1·647 (3)	—O(3)	1·646 (2)
—O(2)	1·648 (2)	—O(4)	1·647 (3)
—O(4^{i})	1·653 (3)	—O(1^{ii})	1·647 (3)
Mean	1·647	Mean	1·645
Na$^+$ coordination			
Na(1)—*W*(3^{iii})	1·20 (2)	—*W*(6)	2·56 (2)
—*W*(3^{iv})	2·38 (2)	—*W*(2)	2·58 (2)
—*W*(5)	2·38 (2)	—O(1^{iv})	2·83 (1)
—*W*(1)	2·38 (2)	—O(5^{v})	3·00 (1)
—O(4^{iv})	2·41 (1)	—O(5^{iv})	3·09 (1)
—*W*(4)	2·52 (2)		

Symmetry code: (i) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, -y, -\frac{1}{2}+z$; (iii) $-x, 1-y, 1-z$; (iv) $x, 1+y, z$; (v) $x-\frac{1}{2}, 1+y, \frac{1}{2}-z$.

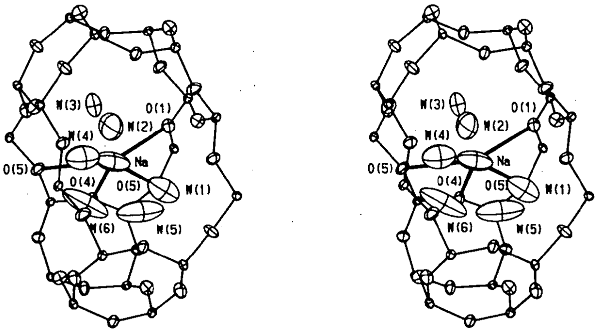

Fig. 1. Coordination of Na$^+$ in Na-P2, seen approximately along **b**. The *c* axis is vertical.

several synthetic phases, *e.g.* Na-P1 and TMA-gismondine. Due to the flexibility of the gismondine framework, the symmetry changes with the composition of the zeolite. Gismondine networks have been refined in a number of different space groups, *e.g.* $I4_1/amd$, $I\bar{4}$, $Pmn2_1$, $I2$, $P2_1/a$; see references cited by Meier & Olson (1987).

The maximum symmetry of the gismondine net is $I4_1/amd$ and *a* and *b* are the pseudo-tetragonal axes in Na-P2. It is thus remarkable that the *b* and *c* axes are of almost equal length in the structure. A similar situation was encountered in connection with an X-ray powder diffraction study of the mineral gobbinsite (McCusker, Baerlocher & Nawaz, 1985).

Typical Al—O and Si—O distances in fully ordered zeolites, like nepheline hydrate I (Hansen & Fälth, 1982), are 1·74 and 1·61 Å, respectively. A comparison of the mean *T*—O distances in Table 1 suggests extensive Si,Al disorder in the present structure model. Interpolation indicates that both tetrahedra contain about 25% Al, corresponding to a framework composition of $Al_4Si_{12}O_{32}^{4-}$. This is in good agreement with the four Na$^+$ ions found in the calculations. Generally speaking, the Al content of Na-P2 frameworks is variable, since a systematic variation in the lattice parameters was observed as a function of starting composition in the syntheses.

An even distribution of cations would lead to the presence of one Na$^+$ ion per cavity (Fig. 1). This Na$^+$ occupies one of the two mirror-related sites present in each cavity. Water molecule *W*(3) is likely to occupy the site which gives a bond distance of 2·38 (2) Å to Na(1), since 1·20 (2) Å is too short (Table 2). Molecules *W*(1), *W*(2) and *W*(4)–*W*(6) are situated in the mirror plane at the center of the cage and their population is approximately 50%. Short water–water distances, such as *W*(1)–*W*(5) 1·18 (4), *W*(4)–*W*(2) 1·55 (3), *W*(4)–*W*(6) 1·79 (4) Å, suggest two alternative arrangements of channel species. In 50% of the cavities *W*(1), *W*(2), *W*(6) are present, while *W*(4) and *W*(5) are present in the other 50%.

We wish to thank the Swedish Natural Science Research Council (NFR) and the National Swedish Board for Technical Development (STU) for financial support and Dr Christer Svensson for helpful discussions throughout this study.

References

Fälth, L. (1981). *Recent Progress Reports and Discussion. Fifth International Conference on Zeolites* 1980, edited by R. Sersale, C. Colella & R. Aiello, pp. 45–48. Napoli: Giannini.

Hansen, S. & Fälth, L. (1982). *Zeolites*, **2**, 162–166.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Lundgren. J.-O. (1982). *Crystallographic Computer Programs.* Report UUIC-B13-04-05. Institute of Chemistry, Univ. of Uppsala, Sweden.

McCusker, L. B., Baerlocher, C. & Nawaz, R. (1985). *Z. Kristallogr.* **171**, 281–289.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Meier, W. M. & Olson, D. H. (1987). *Atlas of Zeolite Structure Types.* London: Butterworth.