

chemical composition of the mineral is slightly richer in Na compared with our structure, their Na(4) site is expected to be substantially vacant by analogy with the structures of the present material and $\text{Na}_6\text{Ca}_3[\text{Si}_6\text{O}_{18}]$ (Ohsato *et al.*, 1985). The fact that they ignored this possibility and did not carry out site-occupancy refinement would presumably explain why they failed to refine the structure in $P3_121$ (or $P3_221$).

We thank Professors H. Minato and T. Sugimura for helpful suggestions, and Drs N. Haga and F. Nishi for valuable discussions. One of the authors (HO) thanks the Ministry of Education, Science and Culture for the leave to carry out this work for a year at the Mineralogical Institute, Faculty of Science, University of Tokyo.

References

BOND, W. L. (1951). *Rev. Sci. Instrum.* **22**, 344–345.

- FISCHER, R. X. & TILLMANN, E. (1983). *Neues Jahrb. Mineral. Monatsh.* **2**, 49–59.
- GLASSER, L. S. D. & MILESON, J. S. (1968). *J. Am. Ceram. Soc.* **51**, 55.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KÖPPEN, N. & PADUROW, N. N. (1958). *Naturwissenschaften*, **45**, 622.
- MAKI, I. & SUGIMURA, T. (1968). *Yogyo Kyokai Shi*, **76**, 144–148.
- MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- MOIR, G. K. & GLASSER, F. P. (1974). *Phys. Chem. Glasses*, **15**, 6–11.
- OHSATO, H., MAKI, I. & TAKÉUCHI, Y. (1985). *Acta Cryst.* **C41**, 1575–1577.
- OHSATO, H., TAKÉUCHI, Y. & MAKI, I. (1986). In preparation.
- SAHAMA, T. G. & HYTÖNEN, K. (1957). *Mineral. Mag.* **31**, 503–510.
- TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
- WYCKOFF, R. W. G. & MOREY, G. W. (1926). *Am. J. Sci.* **12**, 419–440.

Acta Cryst. (1986). **C42**, 937–942

X-ray Structure Refinement of Mesolite

BY GILBERTO ARTIOLI

Istituto di Mineralogia e Petrologia, Università di Modena, Modena, Italy 41100 and Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

AND JOSEPH V. SMITH AND JOSEPH J. PLUTH

Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

(Received 23 October 1985; accepted 21 February 1986)

Abstract. $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30}\cdot 8\text{H}_2\text{O}$, $M_r = 1164.9$, orthorhombic, $Fdd2$, $a = 18.4049$ (8), $b = 56.655$ (6), $c = 6.5443$ (4) Å, $V = 6823.94$ Å³, $Z = 8$, $D_x = 2.27$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.7093$ Å, $\mu = 9.4$ cm⁻¹, spherical crystal, $T = 294$ K, $F(000) = 4688$, $R(F^2) = 0.032$, 5267 reflections. The mesolite structure has complete Si/Al order and the same framework topology as natrolite and scolecite. The Na atom coordinates four O atoms and two water O atoms in a distorted trigonal prism (Na–O 2.40–2.74, Na–OW 2.34 Å) and the Ca atom coordinates four framework O atoms and three water O atoms in a distorted pentagonal bipyramid (Ca–O 2.50–2.54, Ca–OW 2.31–2.36 Å). H atoms were located for each of the four independent water molecules. The hydrogen-bonding system is generally similar to the arrangements found in natrolite and scolecite. The local geometry of the water molecules adapts to the framework distortions.

Introduction. A series of neutron diffraction studies of fibrous zeolites recently produced accurate positions for O and H atoms of the water molecules, as well as for the framework atoms and the extraframework cations [natrolite: Artioli, Smith & Kvik (1984); scolecite: Kvik, Stahl & Smith (1985); edingtonite: Kvik & Smith (1983); thomsonite: Pluth, Smith & Kvik (1985)]. Mesolite has the same framework topology as natrolite and scolecite, and has an intermediate composition near $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30}\cdot 8\text{H}_2\text{O}$ (Alberti, Pongiluppi & Vezzalini, 1982). The similarity of the framework topology and Si/Al order between natrolite, mesolite and scolecite was already postulated by Taylor, Meek & Jackson (1933). The proposed mesolite structure was confirmed by Adiwidjaja (1972) and refined by Pechar (1982) with low-accuracy data. The present X-ray refinement aims to obtain precise coordinates for mesolite, comparable to those of the

Table 1. Final atomic coordinates and B values with estimated standard deviations

B is B_{eq} defined as $\frac{4}{3} \sum_i \sum_j \beta_{ij}(\mathbf{a}_i, \mathbf{a}_j)$ for all atoms except H for which B was isotropically constrained during refinement.

| | x | y | z | B(Å ²) |
|-------|--------------|-------------|--------------|--------------------|
| Si(1) | 0.75000 | 0.75000 | 0.00000 | 0.55 (1) |
| Si(2) | 0.15499 (2) | 0.76432 (1) | 0.87210 (9) | 0.48 (1) |
| Si(3) | 0.90188 (2) | 0.81979 (1) | 0.65040 (9) | 0.50 (1) |
| Si(4) | 0.08794 (2) | 0.84688 (1) | 0.65213 (9) | 0.52 (1) |
| Si(5) | 0.00435 (2) | 0.83180 (1) | 0.27740 (9) | 0.53 (1) |
| Al(1) | 0.78689 (2) | 0.78025 (1) | 0.61310 (9) | 0.50 (1) |
| Al(2) | 0.03630 (2) | 0.80211 (1) | 0.89287 (9) | 0.52 (1) |
| Al(3) | 0.95155 (2) | 0.86233 (1) | 0.89294 (9) | 0.51 (1) |
| O(1) | 0.76818 (5) | 0.77289 (2) | 0.86482 (17) | 1.03 (2) |
| O(2) | 0.02298 (5) | 0.80800 (2) | 0.15228 (17) | 0.98 (2) |
| O(3) | 0.98498 (6) | 0.85319 (2) | 0.12809 (18) | 1.18 (2) |
| O(4) | 0.82365 (4) | 0.80837 (1) | 0.59682 (16) | 0.70 (1) |
| O(5) | 0.07262 (4) | 0.77385 (1) | 0.86425 (17) | 0.72 (1) |
| O(6) | 0.16644 (5) | 0.85935 (2) | 0.67096 (18) | 0.83 (2) |
| O(7) | 0.84335 (5) | 0.75866 (2) | 0.51529 (18) | 1.00 (2) |
| O(8) | 0.09631 (5) | 0.82339 (2) | 0.79447 (17) | 0.93 (2) |
| O(9) | 0.88933 (5) | 0.84183 (2) | 0.80185 (17) | 0.98 (2) |
| O(10) | 0.95568 (5) | 0.80062 (2) | 0.75319 (18) | 1.06 (2) |
| O(11) | 0.20947 (5) | 0.78462 (2) | 0.95950 (17) | 0.86 (2) |
| O(12) | 0.02193 (5) | 0.86358 (2) | 0.71805 (18) | 1.00 (2) |
| O(13) | 0.93735 (5) | 0.82799 (2) | 0.43383 (17) | 1.09 (2) |
| O(14) | 0.18020 (5) | 0.75695 (2) | 0.64166 (17) | 1.06 (2) |
| O(15) | 0.07638 (5) | 0.83892 (2) | 0.41273 (17) | 0.99 (1) |
| Na | 0.96736 (3) | 0.76089 (1) | 0.63172 (14) | 1.48 (1) |
| Ca | 0.22807 (1) | 0.82737 (1) | 0.88068 (9) | 0.91 (1) |
| OH(1) | 0.05347 (7) | 0.76839 (2) | 0.37684 (22) | 1.67 (2) |
| OH(2) | 0.78167 (10) | 0.81598 (3) | 0.07685 (25) | 2.83 (4) |
| OH(3) | 0.20069 (8) | 0.84820 (3) | 0.18338 (23) | 2.46 (3) |
| OH(4) | 0.81793 (6) | 0.85687 (2) | 0.36556 (28) | 2.05 (3) |
| H(11) | 0.0450 (13) | 0.7813 (4) | 0.322 (4) | 0.7 (5) |
| H(12) | 0.0881 (14) | 0.7679 (4) | 0.420 (5) | 0.9 (5) |
| H(21) | 0.7773 (13) | 0.8037 (5) | 0.018 (5) | 1.0 (5) |
| H(22) | 0.8085 (17) | 0.8232 (5) | 0.004 (6) | 2.7 (8) |
| H(31) | 0.2274 (16) | 0.8560 (5) | 0.247 (6) | 2.1 (7) |
| H(32) | 0.1685 (14) | 0.8438 (4) | 0.260 (5) | 1.2 (6) |
| H(41) | 0.8072 (13) | 0.8702 (4) | 0.387 (5) | 0.6 (5) |
| H(42) | 0.8615 (16) | 0.8525 (5) | 0.359 (6) | 2.0 (6) |

other recent refinements of fibrous zeolites. A neutron refinement was excluded because of the large amount of reactor time required for the data collection.

Experimental. The crystal was selected from a sample composed of 2–6 cm long prismatic rods from Poona, India. All crystals showed the (100) or (001) twinning characteristic of mesolite crystals (Hey & Bannister, 1933). A small fragment of a twin was selected under polarized light and ground to a sphere of ~0.4 mm in diameter. Another fragment from the same crystal was analyzed with an electron microprobe (EDS mode, $\text{An}_{70}\text{Ab}_{30}$ standard) and gave an almost ideal composition SiO_2 46.4, Al_2O_3 25.8, CaO 9.9, Na_2O 4.8% (ideal 46.4, 26.3, 9.6, 5.3%), consistent with the observation that zeolites with an ordered framework have a narrow compositional field (Alberti, 1979).

Precession photographs confirmed the space group *Fdd2*. The cell parameters were obtained by a least-squares fit to 20 observed values of 2θ for reflections with $27^\circ < 2\theta < 55^\circ$, each observed value being the corrected angle from the centering of eight forms of the same reflection. The data were collected on a Picker four-circle diffractometer with Krisel automation using $\text{Mo K}\alpha$ radiation. A total of 11 830 diffraction intensities was collected; reciprocal space was explored for

$+h+k+l$ for $3^\circ < 2\theta < 80^\circ$. The scanning technique was $\theta/2\theta$, at a scan rate of 3° min^{-1} and a scan width $\Delta 2\theta = (1 + 0.7 \tan \theta)^\circ$. The relative variation of the standard-reflection intensities remeasured during data collection was less than 1.0%. Lorentz and polarization corrections as well as an absorption correction for a spherical crystal were applied. The computed absorption coefficient gave a constant transmission factor of 0.75. Averaging of 11 568 intensities out to $\sin \theta/\lambda = 0.91 \text{ \AA}^{-1}$ gave 5823 unique diffraction values for the structure refinement. The residual for merging of equivalent reflections was $R = 0.026$. Initial coordinates for the refinement were from Adiwidjaja (1972). The origin was shifted ($x-0.25, y-0.25, z$) to be consistent with the standard cell for the space group *Fdd2* in *International Tables for X-ray Crystallography* (1952). Refinement was straightforward for framework Si, Al and O atoms. An analysis of a difference Fourier synthesis produced the positions for extraframework cations and water O atoms. Successive least-squares and difference Fourier analyses allowed the determination of the H atoms, which were unexpectedly well defined. The eight H atoms were kept isotropic through the refinement. The final cycles of least squares refined one scale factor, one extinction parameter, 108 positional, 172 anisotropic and 8 isotropic thermal parameters (Table 1).^{*} The full-matrix least-squares refinement minimized $\sum [w(F_o^2 - F_c^2)]^2$ with final $w^{-1} = [\sigma(F^2)]^2 + (0.02F^2)^2$. A 3σ cutoff was applied to exclude very weak reflections. The isotropic-extinction correction assumed a type I crystal with a Lorentzian mosaic-spread distribution and followed the Becker & Coppens (1974, 1975) formalism. The final cycle of least-squares refinement gave a maximum $\Delta/\sigma = 0.5$ for a hydrogen B , $R(F^2) = 0.032$, $wR(F^2) = 0.052$, $S = 1.2$ for 5267 reflections used in the refinement and $R(F^2) = 0.035$ for all 5303 reflections. The final difference Fourier synthesis was essentially featureless, with maximum peaks of 0.4 e \AA^{-3} . Neutral scattering factors were used (*International Tables for X-ray Crystallography*, 1974).

A package of crystallographic computer programs from the University of Uppsala, Sweden was used (Lundgren, 1983).

Discussion. Mesolite is structurally related to natrolite and scolecite. In each of these minerals the aluminosilicate framework has exactly the same topology and Si/Al ordering scheme over tetrahedral nodes. The highest possible symmetry for the undistorted tetrahedral framework composed of $T_5\text{O}_{10}$ units is $I4_1/a2/m2/d$ (Alberti & Gottardi, 1975; Smith, 1983),

^{*} Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42846 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

but the symmetry is lowered in the crystal structures by rotation of the chains, ordering of Si/Al on the tetrahedral nodes, and presence of extraframework cations and water molecules. Tetragonal symmetry is found only in tetranatrolite, the disordered form of natrolite (Andersen, Dano & Petersen, 1969; Chen & Chao, 1980). The Si/Al order in the framework of natrolite is accompanied by rotation of the chains and increase in the ($b-a$) value (Alberti & Vezzalini, 1981) and the symmetry of the completely ordered natrolite is orthorhombic $Fdd2$ (Artioli, Smith & Kvik, 1984). In scolecite the cation substitution in the channels: $2\text{Na} \rightarrow \text{Ca} + \text{H}_2\text{O}$ (Alberti, Pongiluppi & Vezzalini, 1982; Kvik, Stahl & Smith, 1985) is associated with reduction of the symmetry to monoclinic pseudo-orthorhombic (Cc). In mesolite (Fig. 1) the alternation of layers of natrolite and scolecite type produces a larger cell with $Fdd2$ symmetry ($b_{\text{mesolite}} = 3b_{\text{natrolite}}$). Each channel in mesolite contains either Na or Ca atoms. The channels are directed along the crystallographic c direction and adjacent channels with the same chemical content form layers parallel to the (010) plane. There is alternation of one natrolite-like layer and two scolecite-like layers along b , with different orientation of the boat-shaped channels in subsequent natrolite layers or pairs of scolecite layers.

Aluminosilicate framework

Mesolite has complete order in the framework tetrahedral sites. The mean tetrahedral distances obtained here (Table 2) match extremely well (maximum difference 0.012 Å) with those obtained for natrolite (Artioli, Smith & Kvik, 1984) and scolecite (Kvik, Stahl & Smith, 1985) with neutron diffraction. Complete order was indicated for both natrolite and scolecite by refinement of neutron scattering lengths for tetrahedral sites. In each tetrahedron of mesolite, the local deviations from regularity coincide with the distortions in the end-member frameworks. An apparent general decrease in the mesolite distances is

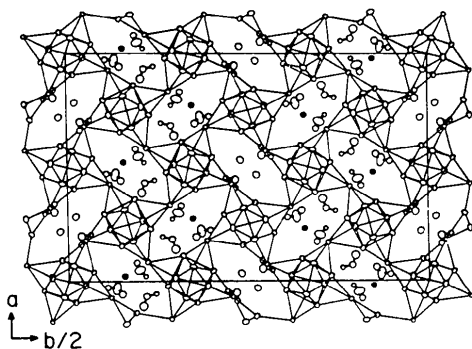


Fig. 1. Projection of the mesolite structure down the c axis. Na atoms are open symbols in the channels, Ca atoms are shaded.

attributed to the thermal motion at 294 K compared with the two neutron studies performed at 20 K. The internal rigidity of the tetrahedra is contrasted with a larger flexibility in the $T-O-T$ angles. The rearrangement of the tetrahedra with respect to each other and the consequential distortion of the chains in response to different chemical content in the channels are responsible for the lowering of the symmetry in mesolite and scolecite relative to natrolite. In natrolite there is only one type of chain, surrounded by four channels

Table 2. Framework geometry: comparison between equivalent distances (Å) and angles ($^\circ$) of mesolite, natrolite and scolecite

| | Mesolite at 294 K (this study) | Natrolite at 20 K (Artioli <i>et al.</i> , 1984) | Scolecite at 20 K (Kvik <i>et al.</i> , 1985) |
|-------------------|-----------------------------------|--------------------------------------------------------|-----------------------------------------------------|
| Si(1)—O(1) | 1.605 (1) | 1.608 (1) | 1.612 (1) |
| Si(1)—O(14) | 1.632 (1) | 1.632 (1) | 1.620 (1) |
| Mean | 1.619 | 1.620 | 1.616 |
| Si(2)—O(5) | 1.610 (1) | 1.621 (1) | 1.614 (1) |
| Si(2)—O(7) | 1.604 (1) | 1.612 (1) | 1.607 (1) |
| Si(2)—O(11) | 1.630 (1) | 1.614 (1) | 1.634 (1) |
| Si(2)—O(14) | 1.632 (1) | 1.641 (1) | 1.633 (1) |
| Mean | 1.619 | 1.622 | 1.622 |
| Si(3)—O(4) | 1.617 (1) | 1.621 (1) | 1.614 (1) |
| Si(3)—O(9) | 1.611 (1) | 1.612 (1) | 1.607 (1) |
| Si(3)—O(10) | 1.617 (1) | 1.614 (1) | 1.634 (1) |
| Si(3)—O(13) | 1.628 (1) | 1.641 (1) | 1.633 (1) |
| Mean | 1.618 | 1.622 | 1.622 |
| Si(4)—O(6) | 1.613 (1) | 1.621 (1) | 1.610 (1) |
| Si(4)—O(8) | 1.632 (1) | 1.612 (1) | 1.630 (1) |
| Si(4)—O(12) | 1.599 (1) | 1.614 (1) | 1.601 (1) |
| Si(4)—O(15) | 1.644 (1) | 1.641 (1) | 1.646 (1) |
| Mean | 1.622 | 1.622 | 1.621 |
| Si(5)—O(2) | 1.615 (1) | 1.608 (1) | 1.612 (1) |
| Si(5)—O(3) | 1.597 (1) | 1.608 (1) | 1.601 (1) |
| Si(5)—O(13) | 1.617 (1) | 1.632 (1) | 1.620 (1) |
| Si(5)—O(15) | 1.645 (1) | 1.632 (1) | 1.642 (1) |
| Mean | 1.619 | 1.620 | 1.619 |
| Al(1)—O(1) | 1.734 (1) | 1.745 (1) | 1.746 (1) |
| Al(1)—O(4) | 1.734 (1) | 1.752 (1) | 1.738 (1) |
| Al(1)—O(7) | 1.728 (1) | 1.741 (1) | 1.754 (1) |
| Al(1)—O(11) | 1.761 (1) | 1.750 (1) | 1.767 (1) |
| Mean | 1.739 | 1.747 | 1.751 |
| Al(2)—O(2) | 1.747 (1) | 1.745 (1) | 1.746 (1) |
| Al(2)—O(5) | 1.745 (1) | 1.752 (1) | 1.738 (1) |
| Al(2)—O(8) | 1.757 (1) | 1.741 (1) | 1.754 (1) |
| Al(2)—O(10) | 1.745 (1) | 1.750 (1) | 1.767 (1) |
| Mean | 1.749 | 1.747 | 1.751 |
| Al(3)—O(3) | 1.736 (1) | 1.745 (1) | 1.746 (1) |
| Al(3)—O(6) | 1.739 (1) | 1.752 (1) | 1.743 (1) |
| Al(3)—O(9) | 1.737 (1) | 1.741 (1) | 1.742 (1) |
| Al(3)—O(12) | 1.730 (1) | 1.750 (1) | 1.747 (1) |
| Mean | 1.736 | 1.747 | 1.745 |
| Si(1)—O(1)—Al(1) | 139.41 (6) | 140.63 (5) | 133.76 (5) |
| Si(5)—O(2)—Al(2) | 132.99 (6) | 140.63 (5) | 133.76 (5) |
| Si(5)—O(3)—Al(3) | 147.97 (7) | 140.63 (5) | 143.93 (5) |
| Si(3)—O(4)—Al(1) | 134.57 (6) | 129.01 (5) | 132.70 (6) |
| Si(2)—O(5)—Al(2) | 131.69 (5) | 129.01 (5) | 132.70 (6) |
| Si(4)—O(6)—Al(3) | 136.78 (6) | 129.01 (5) | 138.18 (6) |
| Si(2)—O(7)—Al(1) | 143.36 (6) | 138.92 (5) | 135.18 (8) |
| Si(4)—O(8)—Al(2) | 135.18 (6) | 138.92 (5) | 135.18 (8) |
| Si(3)—O(9)—Al(3) | 129.42 (6) | 138.92 (5) | 133.43 (8) |
| Si(2)—O(10)—Al(2) | 134.92 (6) | 134.79 (5) | 127.25 (5) |
| Si(2)—O(11)—Al(1) | 126.78 (6) | 134.79 (5) | 127.25 (5) |
| Si(4)—O(12)—Al(3) | 136.31 (7) | 134.79 (5) | 132.29 (6) |
| Si(3)—O(13)—Si(5) | 153.50 (7) | 144.32 (5) | 150.67 (7) |
| Si(1)—O(14)—Si(2) | 144.11 (7) | 144.32 (5) | 150.67 (7) |
| Si(4)—O(15)—Si(5) | 133.22 (6) | 144.32 (5) | 133.19 (7) |

Table 3. *Geometry of the extraframework cations; comparison of cation—O distances (Å) between mesolite, natrolite and scolecite*

| | Mesolite at 294 K (this study) | Natrolite at 20 K (Artioli <i>et al.</i> , 1984) | Scolecite at 20 K (Kvick <i>et al.</i> , 1985) |
|--------------------|-----------------------------------|--------------------------------------------------------|------------------------------------------------------|
| Na—O(5) | 2.571 (1) | 2.500 (1) | |
| Na—O(5) | 2.735 (1) | 2.596 (1) | |
| Na—O(7) | 2.410 (1) | 2.365 (1) | |
| Na—O(10) | 2.397 (1) | 2.391 (1) | |
| Na—O \bar{W} (1) | 2.339 (1) | 2.369 (1) | |
| Na—O \bar{W} (1) | 2.340 (2) | 2.387 (1) | |
| Mean | 2.465 | 2.435 | |
| Ca—O(4) | 2.501 (1) | | 2.478 (1) |
| Ca—O(6) | 2.541 (10) | | 2.589 (1) |
| Ca—O(8) | 2.500 (1) | | 2.507 (1) |
| Ca—O(11) | 2.499 (1) | | 2.531 (1) |
| Ca—O \bar{W} (2) | 2.311 (2) | | 2.313 (2) |
| Ca—O \bar{W} (3) | 2.360 (1) | | 2.351 (1) |
| Ca—O \bar{W} (4) | 2.354 (2) | | 2.351 (1) |
| Mean | 2.438 | | 2.446 |

containing Na atoms; in scolecite there is one different type of chain, distorted with respect to the natrolite chain, surrounded by four channels containing Ca atoms; and in mesolite there are two types of chain, one surrounded by two Na and two Ca channels and the second surrounded by one Na and three Ca channels. This results in large differences between the $T-O-T$ angles of the three structures, with changes as large as 9° . The distortion is particularly evident in the angles associated with O atoms bridging two adjacent chains: the Si(3)—O(4)—Al(1), Si(2)—O(5)—Al(2) and Si(4)—O(6)—Al(3) angles show relatively small differences between mesolite and scolecite (1.87 , -1.01 , -1.40°), but present large deviations between mesolite and natrolite and between scolecite and natrolite (5.56 , 2.68 , 7.77° and 3.69 , 3.69 , 9.17° respectively). The angular range of $T-O-T$ angles is also remarkably larger in mesolite and scolecite (126 – 154 and 127 – 151° respectively) than in natrolite (129 – 144°).

Cation coordinations

Table 3 lists the distances to the Na and Ca atoms. The geometrical arrangements of the cations in the channels closely reflect the ones in natrolite and scolecite. Each Na channel has twice the number of cations as a Ca channel. The Na atoms coordinate four framework O atoms on one side of the tetrahedral spiral forming the channel and two water molecules, one above and one below the tilted plane of the silicate coil (Artioli, Smith & Kvick, 1984, Fig. 2). Each water molecule is shared by two adjacent Na atoms along the channel and the Na coordination polyhedron becomes a distorted trigonal prism. As in natrolite, the prism is distorted because of the longer distances between the cation and the framework O atoms (2.40 – 2.74 Å) with respect to the distances between the cation and the water O (2.34 Å). The longest distances in the polyhedron are those directed to the framework O atoms bridging the chains [Na—O(5) 2.57 – 2.74 Å].

The Ca atoms also coordinate four framework O atoms of the silicate coil but are slightly more centered in the channel than the Na atoms. The Ca atom therefore has similar distances to all four O atoms (Ca—O 2.50 – 2.54 Å) instead of two long and two short distances as the Na atom [Na—O(long) 2.57 – 2.74 ; Na—O(short) 2.40 – 2.41 Å]. Three water molecules complete the hydration polyhedron which could be described as a distorted pentagonal bipyramid (Kvick, Stahl & Smith, 1985). The equatorial plane of the bipyramid is formed by the four framework O atoms and one of the water molecules, situated off the center of the channel on the opposite side with respect to the Ca atom. The other two water molecules, above and below this plane, represent the apices of the bipyramid and are not shared by other cations. The cation—framework-O distances (Ca—O 2.50 – 2.54 Å) are longer than the cation—water-O distances (Ca—O \bar{W} 2.31 – 2.36 Å), similar to what was found in scolecite and in the Na coordination polyhedron. In mesolite, the mean Ca—O distance (2.438 Å) is shorter than the corresponding value in scolecite (2.446 Å), while the mean Na—O distance (2.465 Å) is longer than the value found in natrolite (2.435 Å). The individual differences are more significant for the cation—framework-O distances rather than the cation—water-O distances and cannot be explained by thermal foreshortening at room temperature. This could be an indication that the Ca atom compensation of the residual charges in the framework is more important than the Na compensation, owing to the larger Ca positive charge. This is probably related to the larger distortion of the scolecite framework with respect to natrolite.

Water molecules and hydrogen bonding

All water molecules in the structure participate in the cation coordination and are involved in hydrogen bonds to framework O atoms. All framework O atoms not coordinated to Na or Ca are acceptors of hydrogen bonds. The bonding system is obviously similar to the one already discussed in natrolite and scolecite. The observed differences in O \bar{W} —H and H...O distances and in the internal water molecule angles between the end-member structures and mesolite, are mainly due to the diffraction methods which have been used. It is clear that O \bar{W} —H distances obtained from H-atom positions resulting from X-ray diffraction data are shorter than those obtained from neutron diffraction atomic positions (see for example the discussion in Hamilton & Ibers, 1968). This is mainly due to the aspherical distribution of the hydrogen K electron toward the O atom (Tomii, 1958). Also, the fact that the scattering factor for an isolated H atom is used for X-ray refinement produces abnormally low isotropic thermal parameters with respect to the neutron studies (Jensen & Sundaralingam, 1964). Furthermore, X-ray data

collection at room temperature has produced thermal foreshortening with respect to the neutron data at 20 K. We therefore have to take into account that our OW—H distances are necessarily shorter (~20%) than the corresponding neutron diffraction distances and consequently a parallel increase in the H...O distances is also observed. However, a qualitative comparison among the hydrogen-bonding systems in the three structures is possible (Table 4). The asymmetry of the hydrogen bonds for all of the water molecules is evident except for the water molecule which lies on the equatorial plane of the Ca bipyramid. Both hydrogen bonds formed by OW(4) are relatively strong compared with the range found in zeolites and could be responsible for the large H(41)—OW(4)—H(42) angle (122.9°) found in this water molecule. Also the similarity of these two bonds (2.01–2.03 Å) confirms that no preference is observed for acceptor O atoms linked to one Si and one Al atom with respect to acceptor O atoms linked to two Si atoms [O(3) and O(13) respectively]. This was already observed in scolecite, and confirmed in the present refinement, where OW(3) is forming the stronger hydrogen bond (2.01 Å) to O(15), which is also an Si—O—Si acceptor. These geometrical features suggest that hydrogen bonding has only a secondary influence on the arrangement of the water molecules in the cavity as compared to the major cation—H and framework O—water—O repulsive forces. The smaller H(21)—OW(2)—H(22) angle (102.5°) and the larger H(11)—OW(1)—H(12) and H(41)—OW(4)—H(42) angles (111.7 and 122.9°) with respect to the H—O—H angle for the water molecule in the gas phase (104.5°; Kuchitsu, 1971) follow the variation in the distances between acceptor oxygens [O(1)—O(9) 4.517, O(2)—O(14) 5.196, O(3)—O(13) 5.405 Å].

Thermal analyses of mesolite dehydration show contrasting results between different samples (Koizumi, 1953; Peng, 1955; Van Reeuwijk, 1972; Adiwidjaja, 1972; Alberti, Pongiluppi & Vezzalini, 1982; Gottardi & Galli, 1985) which are not easily explained on the basis of simple crystallographic considerations. However, the major dehydration events at 520, 600 and 670 K probably represent major structural changes. The first peak of the DTG analysis is sometimes a doublet and probably corresponds to the release of the water molecule in the equatorial plane of the Ca bipyramid, as could be inferred by a similar peak in the DTG spectrum of scolecite and correlated with W(4) by a structural study of the partially dehydrated scolecite (Adiwidjaja, 1972).

The peak around 600 K is somewhat similar to the sharp peak found in natrolite and should be related to the release of the water molecule of the Na channel. The last major peak at 670 K should correspond to the loss of the remaining two water molecules in the Ca channel. Reported different dehydration processes could be

Table 4. *Water and hydrogen bonds; comparison between distances (Å) and angles (°) of mesolite, natrolite and scolecite*

| | Mesolite at 294 K (this study) | Natrolite at 20 K (Artioli <i>et al.</i> , 1984) | Scolecite at 20 K (Kvick <i>et al.</i> , 1985) |
|-------------------|-----------------------------------|--------------------------------------------------------|------------------------------------------------------|
| OW(1)—H(11) | 0.83 (2) | 0.974 (2) | |
| OW(1)—H(12) | 0.70 (3) | 0.964 (2) | |
| OW(2)—H(21) | 0.80 (3) | | 0.976 (1) |
| OW(2)—H(22) | 0.80 (3) | | 0.964 (2) |
| OW(3)—H(31) | 0.78 (3) | | 0.967 (2) |
| OW(3)—H(32) | 0.82 (3) | | 0.971 (2) |
| OW(4)—H(41) | 0.79 (2) | | 0.969 (1) |
| OW(4)—H(42) | 0.84 (3) | | 0.950 (2) |
| H(11)—OW(1)—H(12) | 111.7 (2.6) | 107.9 (2) | |
| H(21)—OW(2)—H(22) | 102.5 (3.2) | | 107.3 (2) |
| H(31)—OW(3)—H(32) | 107.0 (3.3) | | 106.6 (2) |
| H(41)—OW(4)—H(42) | 122.9 (2.5) | | 111.1 (2) |
| H(11)...O(2) | 1.92 (3) | 1.877 (2) | |
| H(12)...O(14) | 2.31 (3) | 2.103 (2) | |
| H(21)...O(1) | 2.02 (3) | | 1.746 (1) |
| H(22)...O(9) | 2.25 (3) | | 2.101 (2) |
| H(31)...O(12) | 2.39 (3) | | 2.119 (2) |
| H(32)...O(15) | 1.99 (3) | | 1.828 (2) |
| H(41)...O(3) | 2.01 (2) | | 1.770 (2) |
| H(42)...O(13) | 2.03 (3) | | 2.038 (2) |

attributed to slight chemical variations or to sample impurities. High-temperature crystal study is desirable to verify these speculations.

GA thanks the Centro di Calcolo dell' Università di Modena for computer time. JVS and JJP thank NSF for grants CHE 8405167 and MRL DMR 8216892. P. B. Moore kindly supplied the crystals.

References

- ADIWIDJAJA, G. (1972). Dissertation, Univ. Hamburg, Federal Republic of Germany.
- ALBERTI, A. (1979). *Chem. Erde*, **38**, 64–82.
- ALBERTI, A. & GOTTARDI, G. (1975). *Neues Jahrb. Mineral. Mh.* **9**, 396–411.
- ALBERTI, A., PONGILUPPI, D. & VEZZALINI, G. (1982). *Neues Jahrb. Mineral. Abh.* **143**, 231–248.
- ALBERTI, A. & VEZZALINI, G. (1981). *Acta Cryst.* **B37**, 781–788.
- ANDERSEN, K. E., DANO, M. & PETERSEN, O. V. (1969). *Medd. Groenl.* **181**, 1–19.
- ARTIOLI, G., SMITH, J. V. & KVICK, A. (1984). *Acta Cryst.* **C40**, 1658–1662.
- BECKER, P. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–153.
- BECKER, P. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.
- CHEN, T. T. & CHAO, G. Y. (1980). *Can. Mineral.* **18**, 77–85.
- GOTTARDI, G. & GALLI, E. (1985). *Natural Zeolites*, pp. 48–51. Berlin: Springer.
- HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids*, pp. 63–66. New York: Benjamin.
- HEY, M. H. & BANNISTER, F. A. (1933). *Mineral. Mag.* **143**, 421–447.
- International Tables for X-ray Crystallography* (1952). Vol. I. Birmingham: Kynoch Press.

- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JENSEN, L. & SUNDARALINGAM, M. (1964). *Science*, **145**, 1185–1187.
- KOIZUMI, M. (1953). *Mineral. J.* **1**, 36–47.
- KUCHITSU, K. (1971). *Bull. Chem. Soc. Jpn.*, **44**, 96–99.
- KVICK, A. & SMITH, J. V. (1983). *J. Chem. Phys.* **79**, 2356–2362.
- KVICK, A., STAHL, K. & SMITH, J. V. (1985). *Z. Kristallogr.* **171**, 141–154.
- LUNDGREN, J. O. (1983). *Crystallographic Computer Programs*. Report No. UUIC-B13-4-05, Univ. of Uppsala, Sweden.
- PECHAR, F. (1982). *Acta Montana*, **59**, 143–152.
- PENG, C. J. (1955). *Am. Mineral.* **40**, 834–856.
- PLUTH, J. J., SMITH, J. V. & KVICK, A. (1985). *Zeolites*, **5**, 74–80.
- SMITH, J. V. (1983). *Z. Kristallogr.* **165**, 191–198.
- TAYLOR, W. H., MEEK, C. A. & JACKSON, W. W. (1933). *Z. Kristallogr.* **84**, 373–398.
- TOMIE, Y. (1958). *J. Phys. Soc. Jpn.*, **13**, 1030–1037.
- VAN REEUWIJK, L. P. (1972). *Am. Mineral.* **57**, 499–510.

Acta Cryst. (1986). **C42**, 942–945

Structure of Tetraamminecopper(II) Dipermanganate

BY NIKOLAOS SEFERIADIS, ERICH DUBLER AND HANS R. OSWALD

Institute of Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

(Received 1 August 1985; accepted 21 February 1986)

Abstract. $[\text{Cu}(\text{NH}_3)_4(\text{MnO}_4)_2]$, $M_r = 369.53$, monoclinic, $P2_1/m$, $a = 5.413$ (1), $b = 9.093$ (1), $c = 10.749$ (1) Å, $\beta = 96.18$ (1)°, $V = 526.0$ (2) Å³, $Z = 2$, $D_m(\text{floatation}) = 2.39$, $D_x = 2.33$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 43.1$ cm⁻¹, $F(000) = 366$, $T = 293$ K. $R = 0.024$ with 1123 unique observed reflections. The structure contains isolated units of $[\text{Cu}(\text{NH}_3)_4(\text{MnO}_4)_2]$. The Cu atoms show the usual (4+2) distorted octahedral coordination with four N atoms in the equatorial positions [Cu–N = 2.013 (2), 2.016 (3) Å] and two O atoms from the tetrahedral permanganate groups occupying the axial sites [Cu–O = 2.456 (3), 2.512 (3) Å]. Thermoanalytical results are discussed.

Introduction. Solid-state precursors with cations mixed at the atomic level can serve for the synthesis at moderate temperature of catalytically active mixed metal oxides. As a part of our study of the thermal decomposition of different copper manganese coordination compounds, we prepared crystals of the title compound, a possible precursor for hopcalite-type catalysts.

This complex was first described by Klobb (1890). An unindexed powder diffraction diagram and IR data have been reported by Müller, Bösch, Baran & Aymonino (1973). Since an understanding of the mechanism of structural changes during decomposition requires a knowledge of the crystal structure, it was decided to investigate this phase.

Experimental. A solution of 10 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 40 ml H_2O , cooled in an ice bath, was first treated with an excess of concentrated ammonia. Adding a cold

saturated solution of potassium permanganate yielded a dark-violet precipitation of $[\text{Cu}(\text{NH}_3)_4(\text{MnO}_4)_2]$. Prismatic, twinned crystals could be grown by slow evaporation of a saturated aqueous solution of the above product over concentrated H_2SO_4 at ~278 K. After washing with cold water, ethanol and ether, the crystals were dried in air. They decompose slowly in air at temperatures above 283 K.

For structure determination it was possible to separate a $0.25 \times 0.08 \times 0.12$ mm single crystal, which was mounted in a glass capillary.

Preliminary precession and Weissenberg photographs established symmetry and systematic absences consistent with the monoclinic space groups $P2_1/m$ or $P2_1$. Data collection: Enraf–Nonius CAD-4 diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation; unit-cell parameters and crystal orientation from least-squares refinement of 18 automatically centered reflections in range $25 < 2\theta < 43^\circ$; ω – 2θ scan; total number of reflections measured 4361 (including standards), max. $\sin\theta/\lambda = 0.8063$ Å⁻¹, h –2 to 8, k –2 to 14, l –17 to 17. Intensities and setting angles of six standard reflections monitored at regular intervals; total loss of intensity 3.9% within 82.5 h of exposure time. Intensities reduced to F_o by applying corrections: Lorentz, polarization, linear decay (correction factors 1.00–1.02) and absorption (empirical correction using ψ scans with nine reflections, transmission factors 0.84–1.00).

After averaging of equivalent reflections ($R = 0.017$ on F_{obs}) 2423 unique data remained. 1123 reflections with $I > 2\sigma(I)$ were used for structure determination. Unless otherwise stated, all calculations carried out on a PDP 11/34 computer using Enraf–Nonius CAD-4 *SDP*