Probable Structure of Zeolite Ω

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ZEOLITE Ω[1] is a novel molecular sieve which can be synthesised from alumina–silica gels of suitable composition in presence of appropriate amounts of water, caustic soda, and tetramethylammonium (TMA) hydroxide. Many specimens of the zeolite have been prepared in our laboratory,[2] and certain of these have served to characterise the zeolite by X-ray diffraction, leading to the probable structure which we now report. No preparation contained crystals large enough for single-crystal studies so that it was necessary to use powder photographs only.

The powder pattern was fully indexed on a hexagonal lattice and the unit-cell constants were determined from a Guinier photograph using lead nitrate as standard: $a = 18{\cdot}15 \pm 0{\cdot}2$; $c = 7{\cdot}59 \pm 0{\cdot}01$Å; $V = 2160 \pm 6$Å^3 per unit cell. All the lines of zeolite Ω up to $2\theta = 84°$ were listed, and all could be accounted for with the above unit cell. Another sample of the zeolite was analysed† to give the following results by weight: SiO_2 59·9; Al_2O_3 14·7; Na_2O 7·5; $(TMA)_2O$ 4·7; H_2O 13·3%. The density was measured as 2·13 g. cm.$^{-3}$. Combining these results leads to an approximate unit-cell constant of

$$6{\cdot}8Na^+, 1{\cdot}6\ TMA^+ [Al_8 Si_{28} O_{72}] 21\ H_2O$$

Zeolite Ω, after outgassing, was then found to sorb cyclohexane readily.‡ Thus, like zeolites L,[3,4] X,[5] or Y it must have very wide channels, such as those circumscribed by 12-rings.

Only two hexagonal framework structures could be found which fulfilled the requirements of density and unit cell and which could also sorb cyclohexane. These are structures 1 and 2 considered during the structure determination of Zeolite L.[3] Of these two it was structure 1 which proved to be Zeolite L. This structure is seen in Figure 1a and 7b of ref. 3, while structure 2 is shown in the Figure (a and b) in this communication. Zeolite Ω could therefore be either a slightly modified version of L or it could be the new structure 2.

Initial parameters of framework atoms of zeolite Ω

Atom		Position based on *P*6/*mmm*	*X*	*Y*	*Z*	*B*(Å^2)
Si, Al	1	12 *p*	0·1537	0·4871	0·000	2·0
Si, Al	2	24 *r*	0·0954	0·3569	0·294	2·0
O	1	6 *l*	0·2478	0·4956	0·000	4·0
O	2	6 *l*	0·5821	0·1642	0·000	4·0
O	3	12 *q*	0·1139	0·3860	0·500	4·0
O	4	24 *r*	0·1012	0·4351	0·176	4·0
O	5	12 *o*	0·1665	0·3330	0·224	4·0
O	6	12 *n*	0·0000	0·2735	0·275	4·0

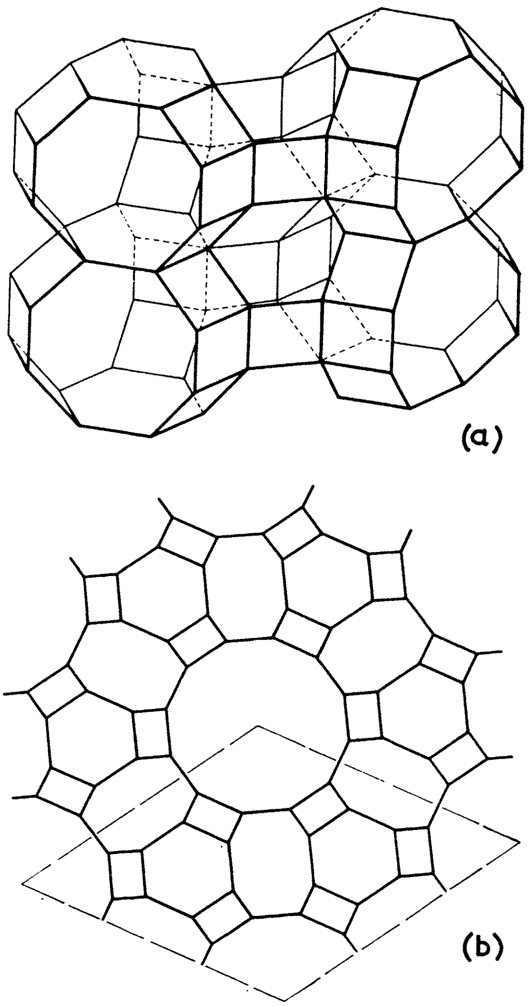

FIGURE. (a) *Framework structure* 2. (b) *Projection in the plane normal to the* c *axis, showing the linking of six gmelinite columns to form the wide central channel. In both* (a) *and* (b) Al *or* Si *is centred at each corner, and the centres of the oxygens lie about halfway between adjacent corners, near but not on the lines connecting corners.*

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† We are indebted to Dr. R. Aiello for this analysis.

‡ The measurements were made by Dr. J. A. Davies in this laboratory.

Zeolite Ω gives strong lines for small angles θ, but above a certain value the lines become weak. For this reason diffractometer intensity measurements had to be limited to 32 lines. Nevertheless, progress was made in differentiating between structures 1 and 2, $R(F)$ for the first Fourier maps being respectively 0·67 and 0·55. Also, based on an assumed symmetry $P6/mmm$, reasonable correlation was found between the Fourier maps calculated for structure 2 and those from the observed powder diffractions but very bad correlation between calculated and 'observed' maps for structure 1 (Zeolite L). Structure 1 was therefore discarded. Subsequent refinement of structure 1 terminated at $R(F) = 0·36$ because of the limited *X*-ray information and consequent poor resolution of the maps, and because $P6/mmm$ has too high a symmetry since oxygens of the 6-rings cannot lie exactly on the mirror plane perpendicular to *c*. TMA$^+$ ions were located but not resolved in gmelinite cages and Na$^+$ at 0, $\frac{1}{2}$, $\frac{1}{4}$ (*i.e.* on sites between gmelinite cages, taking $Z = 0$ as the plane of the 6-ring). Initial co-ordinates are given in the Table.

The *X*-ray information, though unavoidably far from complete, thus accords with structure 2 and so with density, unit-cell, and capacity to sorb cyclohexane. We therefore suggest that structure 2 is the probable structure of zeolite Ω, a member of the extended chabazite group of ref. 3, Table 4.

The framework of Ω is then based upon gmelinite cages (tetradecahedra of Type II[6]). These cages are joined in columns by shared 6-ring faces, the columns running parallel to the *c*-axis. The columns of gmelinite cages are also joined laterally as shown in the Figure to produce restricted cavities between pairs of cages (containing Na$^+$ ions as already indicated). The lateral joining of six such columns creates wide channels running parallel to *c* and having free dimensions almost identical with those in zeolite L (*ca.* 7·5 Å), and circumscribed by 12-ring windows. Indeed the projection of the Ω structure onto a plane normal to *c* is the same as the projection of the structure of L, (*cf.* Figure 7b, ref. 3). The Ω structure has a double system of channels, one system parallel to *c* and easily able to sorb large molecules such as cyclohexane. There is no way in which these wide channels could be blocked by stacking faults. A second channel system involves only the gmelinite cages and the cavities linking them (Figure). It is much more restricted, is two-dimensional in character, and runs in planes normal to *c*. There is no easy passage from one of these layers of channels normal to *c* to layers above or below.

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