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The Crystallographic Determination of the Sorption Sites for Ethyne in Zeolite 4A

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Summary Ethyne molecules are crystallographically found to be physically sorbed by ion to induced-dipole forces at two, and probably three, non-equivalent sites in the sodium form of zeolite A.

Single crystals of zeolite 4A[1] were prepared by a modification of Charnell's method[2] which yielded clear cubes up to 0·075 mm on an edge. Elemental analysis, and the crystal structure determination of a dehydrated crystal,[3] indicate that the formula per unit cell in the space group *Pm*3*m* is $Na_{12}Al_{12}Si_{12}O_{48}$ for the uncomplexed zeolite. A single crystal was dehydrated at 3×10^{-6} Torr and 350° for 48 h and was then exposed to zeolitically dried 99·6% pure ethyne gas at 650 Torr for 20 h at 25°. Approximately six molecules of ethyne are sorbed per unit cell under these conditions.[4] The crystal in its glass capillary was sealed off from the vacuum system and remained isolated from the atmosphere throughout subsequent examination.

A Syntex four-circle autodiffractometer with monochromatized Mo-K_α radiation and a pulse-height analyzer was used throughout. The least-squares cell constant is 12·260(5) Å at 20°, the temperature at which diffraction intensities were measured. Of the intensities measured at the 888 reciprocal lattice points for which $0 < 2\theta < 70°$, only 171 were significant at the 3σ level, where σ is the standard deviation of each observation. Initial approximate atomic positions for Si, Al, O, and Na from previous related structures[3,5] refined quickly to an *R* index of 0·078. A difference Fourier synthesis and subsequent least-squares refinement of positional, thermal and occupancy parameters gave the locations of the ethyne carbon atoms in the structure. The final *R* index is 0·062.

The structure of the aluminosilicate framework is qualitatively the same as had been reported previously.[1] However, the twelve sodium ions are distributed among three equipoints in this structure. Eight Na^+ ions fill a Wyckoff 8(*g*) position, Na(1), on the three-fold axes of the unit cell at $x = 0{\cdot}204$, near to the centres of the six-oxygen windows (twelve-membered rings). In the Figure, these eight ions, only one of which is labelled, can be readily identified because the principal axes of their thermal ellipsoids are not orthogonal to the edges of the unit cell. Three Na^+'s are

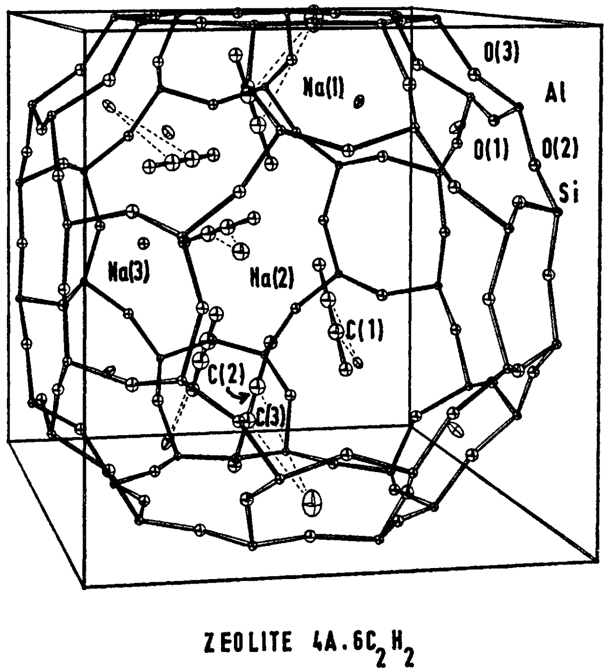

Figure. Zeolite 4A·6CH$_2$

located in the planes of the eight-oxygen windows (sixteen-membered rings) at a Wyckoff 12(*i*) position, Na(2), with $x = 0{\cdot}430$. These are arbitrarily placed at the top, bottom and back faces of the Figure. Each eight-oxygen window contains one Na(2) ion; although positions for others are available, packing considerations prohibit the presence of more than one per window. The remaining single Na^+ is distributed over a twelve-fold equipoint, Na(3), at Wyckoff position 12(*j*) with $x = 0{\cdot}270$, on a two-fold axis normal to the four-oxygen window (eight-membered ring).

Six ethyne molecules are found at two non-equivalent sorption sites in the zeolite 4A structure. Three molecules are symmetrically associated with Na(1) ions (see Figure) such that each carbon atom, C(1), of each molecule is 2·8(1) Å from the cation. The remaining three ethyne molecules are asymmetrically associated with Na(2) ions at distances of 3·0(1) Å for C(2) and 2·6(1) Å for C(3). In each case the cation approaches the ethyne molecule equatorially, indicating that the principle interaction is between the cationic charge and the laterally polarizable π-electron system of the unsaturated hydrocarbon, in agreement with various previous results.[6] Significant contacts between ethyne hydrogen atoms and framework oxygen atoms are entirely absent. Each Na(2) ion is associated with a sorbed molecule, indicating that this site is energetically more favourable than the one involving Na(1), which is only partially filled.

It is expected that the single Na^+ ion at Na(3) has disrupted this structure to some extent. This position is the least stable[3] one for Na^+ in the structure and accordingly the tendency for Na(3) to stabilize itself through complexation should be greatest. Na(3) has moved 0·9 Å further from its four nearest oxygen neighbours in the dehydrated structure, indicating that it does participate in ethyne complexation. In fact it may approach C(2) and C(3) each at 2·6(1) Å, although at the low occupancies present here, this approach must be inaccurately described at best, for it involves only one molecule. Apparently, then, three non-equivalent sorption sites for ethyne exist at a loading corresponding to six molecules per unit cell, and each site is associated with at least one sodium ion.

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