An X-Ray Diffraction Study of the Zeolite Complex *m*-Dichlorobenzene–Nickel Faujasite

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Abstract: The structure of the zeolite complex *m*-dichlorobenzene–nickel faujasite has been studied using single-crystal X-ray techniques. An analysis of the low-order data, using formulas for the average scattering of X-rays from species in various forms of uniform distribution, shows that the sorbed organic molecules form a liquid or near-liquid in the intracrystalline channels. The situation regarding the located nonframework species is similar to that for hydrated natural faujasite.

The ability of highly crystalline zeolites to function as catalysts and as molecular sieves is well known. The faujasite types have been the ones most widely used in connection with catalytic applications, because of their large channels and connecting apertures and because of their good thermal and mechanical stability. As a consequence, the study of structural relationships between the frameworks of these zeolites and their exchangeable cations and sorbed guest molecules is of considerable theoretical interest.

Several investigators have reported on the positions of the partially ordered exchangeable cations in hydrated and dehydrated faujasite-type zeolites and on the positions of the partially ordered water molecules in the hydrated structures.[1-6] To our knowledge, however, no attempt has yet been made to locate sorbed organic species and exchangeable cations in a loaded faujasite-type structure and to determine whether they exist in the channels as crystallographically ordered molecules or are randomly distributed and form essentially a liquid phase.

Experimental Section

A hemispherical, dehydrated, nickel-exchanged single crystal of natural faujasite ion-exchanged by the method reported by Olson[6] was placed in a thin glass capillary and exposed to *m*-dichlorobenzene vapors for 1 month. The capillary was then sealed with a small torch. The probable unit cell content of the resulting complex was estimated to be $(\mathrm{NiO})_{28.5}(\mathrm{Al_2O_3})_{28.5}(\mathrm{SiO_2})_{133}\cdot 24\text{–}32$(*m*-dichlorobenzene). The estimate of the number of sorbed *m*-dichlorobenzene molecules is an extrapolation of the results of a similar experiment by Olson, in which it was found that CoX zeolite sorbed 24–32 molecules of *m*-dibromobenzene per unit cell.[7]

Oscillation and Weissenberg photographs of the complex disclosed that the unit cell was cubic and that the crystal was aligned along [110]. The systematic extinctions were *hkl* when *h*, *k*, and *l* were mixed, and *hk*0 when $h + k \neq 4n$. The diffraction symmetry was m3m. The space group for the complex is thus Fd3m, the characteristic space group for faujasite structures. The lattice constant was found to be 24.45 (1) Å, from a least-squares analysis of data from a 0-level Weissenberg photograph made with Cu Kα radiation (λ 1.54178 Å).

The crystal was transferred to a Philips automatic diffractometer PAILRED, retaining the [110] alignment. Using a 3° (6 mm) counter aperture and monochromatized Cu Kα radiation, automatic runs were made on one-half of each of the reciprocal lattice levels 0 through 15 of the pseudotetragonal unit cell to $\Upsilon = 130°$. Background was measured for 1 min on either side of each peak, and the peaks were scanned at a rate of 1°/min. A total of 5357 intensities was collected. The scan range varied from 2° for the lowest levels to 5° for the low Υ regions of the highest levels.

A reflection was considered to be statistically observed if the relative counting error, $\Delta I/I$,[8] was less than 0.33. Lorentz and polarization corrections were applied to the intensities and approximate absorption corrections were made with the program by Burnham,[9] by using a 17-face approximation for the shape of the 0.2-mm diameter hemispherical crystal. The linear absorption coefficient for the crystal was 80 cm^{-1} for Cu Kα radiation. The transmission factors ranged from 0.33 to 0.52. The error resulting from the 17-face approximation of the crystal shape is estimated to range from 10% for the smallest transmission factors to 2% for the largest ones, with the average over-all error estimated to be about 3–4%.

For each set of space-group-equivalent structure amplitudes in the processed data deck, a weighted average amplitude, $\overline{|F|}$, was calculated using as weighting factors the estimated standard deviations for the equivalent reflections involved, and a weighted average standard deviation, $\bar{\sigma}$, was computed using the individual structure amplitudes as the weighting factors. The original estimated standard deviations used in these calculations were computed according to the formula

$$\sigma(|F|) = \left\{\left(\frac{|F|}{2I_c}\right)^2\left[I + \left(\frac{B_1 + B_2}{2}\right)\left(\frac{t_p}{t_b}\right) + 0.0004(I_c{}^2)\right]\right\}^{1/2}$$

where $\sigma(|F|)$ is the estimated standard deviation of the structure amplitude, I_c is the background-corrected intensity, I is the total intensity, B_1 and B_2 are the background counts on either side of the peak, and (t_p/t_b) is the ratio of the peak counting time to the background counting time. The term $[0.0004(I_c{}^2)]$ allows for errors such as variation in the beam intensity and absorption errors. The average values $\overline{|F|}$ and $\bar{\sigma}$ were retained to represent the independent reflection in question if $\overline{|F|} > 3\bar{\sigma}$. The total number of averaged independent amplitudes retained was 261.

Refinement of the Zeolite Framework and the Partially Ordered Nonframework Species

Starting with the coordinates of the framework atoms in dehydrated nickel(II) faujasite,[6] two cycles of least-

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[1] G. Bergerhoff, W. H. Baur, and W. Nowacki, *Neues Jahrb. Mineral. Montash.*, 193 (1958).

[2] W. H. Baur, *Am. Mineralogist*, **49**, 697 (1964).

[3] L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, **82**, 1041 (1960).

[4] J. V. Smith, J. M. Bennett, and E. M. Flanigen, *Nature*, **215**, 241 (1967).

[5] D. H. Olson, G. T. Kokotailo, and J. F. Charnell, *ibid.*, **215**, 270 (1967).

[6] D. H. Olson, *J. Phys. Chem.*, **72**, 4366 (1968).

[7] D. H. Olson, personal communication.

[8] M. Mack, *Norelco Reptr.*, **12**, 40 (1965).

[9] C. W. Burnham, "An IBM 709/7090 Computer Program for Computing Transmission Factors for Crystals of Essentially Arbitrary Shape," Geophysical Laboratory, Carnegie Institute of Washington, Washington, D. C., 1963.

squares refinement on the scale factor resulted in $R = 0.32$ and $wR = 0.38$; ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{1/2}$, $w = 1/\sigma^2$, function minimized $= \Sigma w(|F_o| - |F_c|)^2$). A Fourier synthesis based on these parameters disclosed, in addition to the framework atoms, about ten electrons in site I′, six electrons in site II′, and four electrons in site II. The likely occupant of site I′ is Ni. On the basis of Olson's results for dehydrated nickel faujasite,[6] site II′ was assumed to be partially occupied by H_2O and site II to be partially occupied by Ni. (The occupants of sites I′, II′, and II will respectively be referred to hereafter as Ni2, OW3, and Ni4.) No other peaks were found in the Fourier synthesis representing more than about 0.5 e/Å^3, suggesting that the sorbed *m*-dichlorobenzene molecules as well as the Ni atoms unaccounted for at this point were probably uniformly distributed in the channels of the faujasite structure. Inclusion of Ni2, OW3, and Ni4 in the model, followed by four cycles of refinement on the occupancy factors for these species, resulted in $R = 0.22$ and $wR = 0.23$.

After an unsuccessful attempt to refine the structure further, it was noted that substantial discrepancies existed between $|F_o|$ and $|F_c|$ for the low-order reflections 220, 222, 311, and 331. Because the $|F_o|$'s for these reflections were comparatively small, and because such discrepancies did not exist for the intense reflections, extinction was not considered to be the cause of these differences.

An atom uniformly distributed according to some radial distribution function having a radius comparable with that of the supercage will contribute significantly only to the low-order structure factors.[10] Consequently, the discrepancies between $|F_o|$ and $|F_c|$ in the low-order data were interpreted as a further indication that the *m*-dichlorobenzene molecules and unlocated Ni atoms are uniformly distributed in the zeolitic channels.

The data for reflections 220, 222, 311, and 331 were then removed from the data deck and the scale factor was re-refined. Four cycles of refinement on the coordinates then resulted in $R = 0.100$ and $wR = 0.101$. Eight cycles of refinement on the occupancy factors of Ni2, OW3, and Ni4 followed by eight more cycles on the isotropic thermal parameters for all species gave $R = 0.100$ and $wR = 0.099$.

A difference Fourier synthesis calculated with the parameters from the last refinement showed no detail of structural significance. The highest peaks above background represented about 0.3 e/Å^3, and appeared to result from anisotropy of the Ni2 electron density toward the center of the nearest hexagonal prisms. However, no anisotropy was evident for any other atom in the structure. Because of this, and because of the relatively small amount of data, the use of anisotropic thermal parameters in the refinements was not attempted. The final value for the standard deviation of an observation of unit weight was 3.50.

As a check on the refinements described above, a similar series of refinements was carried out with a data set obtained using a relative counting error of 1.00 rather than 0.33 as the rejection criterion in processing the intensities. This data set contained 472 averaged, independent reflections. The final parameters obtained from these refinements did not differ from those obtained with the previously described refinements by more than one estimated standard deviation. The final R values were $R = 0.167$, $wR = 0.118$, and $R(F^2) = 0.180$, and the standard deviation of an observation of unit weight was 2.85. The comparable values of R and $R(F^2)$ indicate that a large number of reflections in this data set have amplitudes nearly equal to their standard deviations.[11] Consequently, the smaller data set was used in developing the uniform distribution model described below.

A bond angle calculation made with the refined coordinates disclosed that the mean (Si,Al)–O–(Si,Al) angle was 141 ± 2°. This value is in agreement with the value for fully hydrated faujasite but not with the value for dehydrated nickel(II) faujasite (~138°),[6] suggesting further that the faujasite framework in this complex is probably fully loaded.

Development of the Uniform Distribution Model

A general description of the analysis which led to the final uniform distribution model is given in this section. A detailed explanation of the trials made, of the types of preferred orientation investigated, and of the scattering equations used for the uniformly distributed species in the various trial models are given by Simpson.[12]

In this discussion the value of R for the 16 low-order reflections in Table I will be denoted by R_{16}.

Table I. Low-Order Structure Factor Data for *m*-Dichlorobenzene–Nickel Faujasite[a]

hkl	$\lvert F_o\rvert$	F_c	$(\lvert F_o\rvert - \lvert F_c\rvert)$
220	91	411	−320
222	64	−111	−47
311	240	351	−111
331	487	−667	−182
333	143	157	−15
400	235	−271	−35
440	774	−787	−13
444	325	−299	25
511	459	507	−48
533	1014	−938	77
551	302	300	1
555	1533	−1421	111
620	355	266	89
622	191	−119	71
642	587	−509	78
660	583	712	129

[a] Uniformly distributed atoms are not included in F_c.

After the refinements described above, reflections 220, 222, 311, and 331 were included in the data deck. Refinement of the scale factor then resulted in $R = 0.109$, $wR = 0.145$, and $R_{16} = 0.183$.

On the assumption that the discrepancies between the low-order $|F_o|$ and $|F_c|$ were due to uniformly distributed electron density in the cages, structure factors were calculated for one, three, and four *m*-dichlorobenzene molecules per supercage, uniformly distributed as molecules and as individual carbon and chlorine atoms throughout, and on the surface, of spheres of 0–6-Å

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(10) R. W. James, "The Optical Principles of the Diffraction of X-rays," Vol. II, "The Crystalline State," G. Bell and Sons Ltd., London, 1950, Chapter IX.

(11) W. C. Hamilton, *Norelco Reptr.*, **12**, 31 (1965).

(12) H. D. Simpson, Ph.D. Dissertation, The University of Texas at Austin, 1969.

radii centered in these cages, at intervals of 0.5 Å in the radii. These contributions were added to the corresponding structure factors for the located species, and resultant R values were obtained. Although several of the R values were not significantly different from each other, a minimum R appeared as a function of the radius of distribution in each case. The lowest minima were $R = 0.105$ and $R = 0.106$ for four and three molecules of *m*-dichlorobenzene, respectively, in the supercage, in which the molecules were randomly oriented with their centers distributed throughout a sphere of 5.0-Å radius. The minimum value of R for one molecule per supercage was 0.107, with the individual carbon and chlorine atoms distributed throughout a sphere of 5.0-Å radius. The R_{16} values for these models were 0.150, 0.158, and 0.169, respectively, indicating that although the over-all fit of the data is about the same with all these models, the one based on four molecules per supercage provides the best fit of the low-order data. In view of these results, trials for two molecules per supercage were not conducted.

The two molecular models extend electron density to a distance of 9–10 Å from the centers of the supercages (5 Å plus the radius of a *m*-dichlorobenzene molecule, $\sim$4–5 Å), about 2–3 Å in excess of the free radius of the cage. This was not considered to be a serious drawback for these models because the confining framework oxygen atoms of the supercages define only about 40% of the surface of the spheres used to approximate the shape of these cages. The results for the molecular models can therefore be interpreted to mean that electron density probably exists in the substantial openings between supercages to form a continuum in the zeolite channels. Also, these models probably attempt to account for some electron density in the sodalite cages resulting from the unlocated Ni atoms.

Since calculations with four molecules per supercage provided the best fit of the low-order data and since it was previously estimated that three to four molecules existed in each supercage, it was decided to use four molecules of *m*-dichlorobenzene per supercage as a basis for extending the calculations to include the unlocated Ni. Assuming that partially occupied sites I′ and II contain only Ni, about 14 Ni atoms remained unaccounted for at this stage.

Since the free radius of a sodalite cage is about 3.3 Å, it was decided to use 2.3 Å as the radius of distribution for this cage. Structure factors and values of R, wR, and R_{16} were then calculated for many trial models in which the 14 unlocated Ni atoms were distributed throughout the sodalite and supercages in various proportions and in which four *m*-dichlorobenzene molecules were distributed in each supercage completely uniformly as well as with various kinds of preferred orientation. Thermal parameters of $B = 3.0$ Å^2 were arbitrarily used for the uniformly distributed species in these calculations. The most satisfactory models emerging from these trials all postulated an essentially uniform distribution of electron density in each supercage corresponding to about four molecules of *m*-dichlorobenzene plus one Ni atom, and a uniform distribution of electron density in each sodalite cage corresponding to about one Ni atom. The values of R for the best models ranged from 0.101 to 0.103, and the values of wR ranged from 0.106 to 0.110. The values of R_{16} ranged from 0.121 to 0.135.

Three reflections, 222, 333, and 511, showed poor agreement between $\overline{|F_o|}$ and F_c even with the most satisfactory models. The 333 and 511 reflections have the same value of $\sin \theta/\lambda$, suggesting that one or more of the distribution functions used in the models probably needed to be modified. Also, no contribution is made to F_{222} by the equipoints representing the centers of distribution in the supercages and sodalite cages, Fd3m Wyckoff positions "b" and "a," respectively. Thus, none of the distributions considered affected F_{222}.

A set of equipoints not previously considered as centers of distribution, and which does make a contribution to F_{222}, is the set representing the centers of the hexagonal prisms, Wyckoff position "c." The placement of electron density equivalent to 0.14 Ni in each of these positions and distributed uniformly throughout a sphere of 1.5-Å radius provided a good fit for $\overline{|F_o|}_{222}$ and slightly improved the fit of $\overline{|F_o|}_{333}$ and $\overline{|F_o|}_{511}$ without significantly changing the fit of the other reflections. A more detailed study of the contribution to the low-order structure factors of the average scattering from *m*-dichlorobenzene molecules distributed as molecules and as individual atoms in the supercages indicated that an improved fit of the low-order data, and particularly of $\overline{|F_o|}_{333}$ and $\overline{|F_o|}_{511}$, would be afforded by a model in which the *m*-dichlorobenzene molecules are represented as individual carbon and chlorine atoms with their centers uniformly distributed throughout spheres of 5.8-Å radius in the supercages and with high thermal parameters, $B \approx 20$ Å^2. A further improvement was made by using a radius of distribution of 3.5 Å for the Ni in the supercages.

No discernible physical significance is lost by using an atomic rather than a molecular distribution model, because any model which postulates an essentially uniform distribution of the specified quantities of electron density in the cages fits the data reasonably well. Also, the spherical distribution models are themselves only approximately correct, and the geometrical relationship, if any, of the uniformly distributed Ni to the *m*-dichlorobenzene molecules is unknown.

A structure factor calculation for the model incorporating the above changes and using a thermal parameter of 20 Å^2 for each uniformly distributed species gave $R = 0.102$ and $wR = 0.104$. The improved value for wR suggested that an improved fit of the more reliable low-order reflections had been obtained and that subsequent re-refinement of the parameters for the located species would probably provide a further improvement in the fit of the data. Such a refinement resulted in $R = 0.098$ and $wR = 0.099$. The standard deviation of an observation of unit weight was 3.84.

A linear hypothesis test[13] based on wR indicated that the inclusion of the 30 additional parameters required to describe the uniformly distributed species was justified at the 0.005 level of significance.

The final parameters for this complex are shown in Table II. The bond distances and angles for the located atoms are given in Table III. A table of the $\overline{|F_o|}$ and the final F_c values is available from the authors. The form of the scattering factor used for the uniformly distributed species was $f' = f[3/(\mu R)^3][\sin (\mu R) - \mu R \cos (\mu R)]$, where f is the usual scattering factor as given

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(13) W. C. Hamilton, *Acta Cryst.*, 18, 5021 (1965).

Table II. Final Parameters for *m*-Dichlorobenzene–Nickel Faujasite[a]

Atom	Wyckoff notation	Occupancy factor	*x*	*y*	*z*	*B*, Å^2
(Si,Al)	192(i)	1	−0.0528 (3)	0.0365 (3)	0.1254 (4)	1.6 (1)
O1	96(h)	1	−0.104 (1)	0.104 (1)	0	3.4 (4)
O2	96(g)	1	−0.002 (1)	−0.002 (1)	0.1442 (6)	2.8 (4)
O3	96(g)	1	0.173 (1)	0.173 (1)	−0.0291 (6)	2.3 (4)
O4	96 (g)	1	0.177 (1)	0.177 (1)	0.3232 (7)	2.0 (3)
Ni2	32(e)	0.39 (1)	0.073 (2)	0.073 (2)	0.073 (2)	5.3 (5)
OW3	32(e)	0.75 (5)	0.165 (3)	0.165 (3)	0.165 (3)	3 (1)
Ni4	32(e)	0.08 (1)	0.251 (5)	0.251 (5)	0.251 (5)	3 (2)
C	8(b)	24	$^3/_8$	$^3/_8$	$^3/_8$	20
Cl	8(b)	8	$^3/_8$	$^3/_8$	$^3/_8$	20
NiR1	8(b)	0.86	$^3/_8$	$^3/_8$	$^3/_8$	20
NiR2	8(a)	0.59	$^1/_8$	$^1/_8$	$^1/_8$	20
NiHEX	16(c)	0.14	0	0	0	20

[a] The space group is Fd3m with origin at center of symmetry, and a_0 = 24.45 (1) A. The probable unit cell contents are $(\mathrm{Ni})_{28.5}(\mathrm{SiO_2})_{135}(\mathrm{AlO_2})_{57}\cdot 32\mathrm{C_6H_4Cl_2}$. The numbers in parentheses in the table are estimated standard deviations applicable in the last digit of the corresponding parameters. NiR1 denotes the uniformly distributed Ni in the supercage, NiR2 denotes the uniformly distributed Ni in the sodalite cage, and NiHEX denotes the uniformly distributed Ni in the hexagonal prism.

Table III. Final Interatomic Distances and Angles for *m*-Dichlorobenzene–Nickel Faujasite[a]

Atom set	Distance, Å	Atom set	Angle, deg
(Si,Al)–O1	1.62 (4)	O1–(Si,Al)–O2	111 (2)
(Si,Al)–O2	1.62 (4)	O1–(Si,Al)–O3	112 (2)
(Si,Al)–O3	1.65 (4)	O1–(Si,Al)–O4	108 (2)
(Si,Al)–O4	1.62 (4)	O2–(Si,Al)–O3	106 (2)
O1–O2	2.68 (5)	O2–(Si,Al)–O4	109 (2)
O1–O3	2.71 (5)	O3–(Si,Al)–O4	110 (2)
O1–O4	2.63 (5)	(Si,Al)–O1–(Si,Al)	143 (2)
O2–O3	2.62 (5)	(Si,Al)–O2–(Si,Al)	144 (2)
O2–O4	2.65 (5)	(Si,Al)–O3–(Si,Al)	138 (2)
O3–O4	2.67 (5)	(Si,Al)–O4–(Si,Al)	139 (2)
Ni2–OW3	2.3 (2)	O3–Ni2–O3	94 (3)
Ni2–O2	3.1 (1)	OW3–Ni2–OW3	74 (5)
Ni2–O3	2.5 (1)	O3–Ni2–OW3	95 (4)
OW3–OW3	2.8 (1)	Ni2–OW3–Ni2	104 (5)
OW3–O2	3.0 (1)	O2–Ni4–O2	91 (7)
Ni4–O2	2.6 (2)		
Ni4–O4	3.1 (2)		

[a] The numbers in parentheses are estimated standard deviations.

in the International Tables,[14] $\mu = 4\pi \sin \theta/\lambda$, and *R* is the radius of distribution for the particular species.

Atomic rather than ionic scattering factors were used in all of the calculations described above. Ionic scattering factors differ from those for the corresponding neutral atoms only in the low-angle scattering region, the region of significant contribution by the uniformly distributed species on which the previously described models are based. A repeat series of least-squares refinements was therefore conducted using the located species and scattering factors for Si^{3+}, Al^{0}, O^{-}, and Ni^{2+}, and with the low-order data included, in order to evaluate the assumption of about 50% ionization in fitting the lower order data. These refinements ultimately resulted in $R = 0.105$ and $wR = 0.125$. A comparison of the results obtained for the low-order reflections with the analogous results obtained with the atomic model indicated that about 70% of the uniformly distributed scattering matter required for the atomic model would still be required if the framework atoms are 50% ionized. Accordingly, exactly the same uniform distribution parameters obtained with the atomic model were incorporated into this model, except that three molecules of *m*-dichlorobenzene rather than four were assumed to be distributed throughout the supercage. This resulted in $R = 0.100$ and $wR = 0.102$. Re-refining the parameters for the located species then resulted in $R = 0.099$ and $wR = 0.101$. The standard deviation of an observation of unit weight was 3.91.

The difference in the amount of scattering matter required for the atomic and the ionic models may represent the limit of accuracy in the analysis of the low-order data.

Discussion

The results of this study show that the sorbed organic molecules form a liquid in the supercages which are defined by the aluminosilicate framework of the well-known faujasite structure. Various models for the distribution of *m*-dichlorobenzene were used in the calculation of structure factors and the best fit for the data was obtained when the atoms constituting four molecules were uniformly distributed throughout a sphere of 5.8 Å radius inside each supercage. This radius of distribution extends electron density into the openings connecting the supercages so that a continuum of electron density exists throughout the intracrystalline channels formed by the interconnected supercages. The Ni^{2+} ions which were not definitely located in the structure are randomly distributed in about equal amounts between the supercages and sodalite cages. No organic molecules exist in the sodalite cages because of size limitations of the openings of these cages. The liquid nature of the sorbate prevents any conclusions regarding the bonding. The oxygen surfaces carry a net negative charge which is balanced by the exchangeable cations, and from the X-ray diffraction results it is impossible to decide whether the organic molecules are held to the negative surfaces, form a coordination sphere around a cation, or both. Other techniques will have to be employed to answer these questions.

The arrangement of species in the sodalite cage is the same as in hydrated natural faujasite.[2] The ratio of the occupancy factors for sites I′ (Ni2) and II′ (OW3) is 1:2, and the bond distances are in good agreement with those for the hydrated structure. However, the extent to which these sites are occupied in the present structure is less than for hydrated faujasite. This may be

(14) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962.

due to a different extent of dehydration, or to an association of some of the residual water molecules with the sorbed *m*-dichlorobenzene molecules or with cations which are in turn associated with the sorbed molecules.

The anisotropy of Ni2 in the direction from that site toward the center of the nearest hexagonal prism may be the result of the inability of the small Ni^{2+} ion to be simultaneously coordinated to equal extents by the O atoms in the hexagonal prism six-ring and the adjacent OW3 entities. Such a situation would be in line with that found by Olson[6] in the site I′ region in dehydrated nickel faujasite.

The occupant of site II (Ni4) is uncertain because of the small occupancy factor. The bond distance Ni–O2 ≈ 2.6 Å is about halfway between the values found in hydrated natural faujasite and dehydrated nickel faujasite, suggesting that this site may be about equally occupied by residual water and Ni^{2+} in the present structure, or that the bonding of Ni^{2+} in this site is weakened by association with the sorbed species.

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An X-Ray Diffraction Study of the Zeolite Complex 1-Chlorobutane–Manganese Faujasite

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Abstract: The structure of the zeolite complex 1-chlorobutane–manganese faujasite has been studied using single-crystal X-ray techniques. The application of formulas for the average scattering of X-rays from species uniformly distributed in a spherical volume shows that the zeolite is only about half-saturated. The situation in the sodalite cage is similar to that for hydrated natural faujasite and *m*-dichlorobenzene–nickel faujasite.

In a previous paper[1] we presented a structural investigation of an organic faujasite complex which was prepared by sorbing *m*-dichlorobenzene into a nickel faujasite single crystal. The analysis showed that 24–32 organic molecules and about 7 nickel ions were randomly distributed in the supercages in each unit cell. Concurrently with this investigation we also studied another organic faujasite complex which was prepared by sorbing 1-chlorobutane into a single crystal of manganese faujasite. This paper presents the results of the study of this complex.

Experimental Section

An irregularly shaped single crystal of natural faujasite (encompassing dimension ~0.2 mm) was batch ion-exchanged at 100° for 33 days in a solution 0.35 *M* in $Mn(CH_3CO_2)_2$ and 0.15 *M* in $MnSO_4$, while nitrogen gas was bubbled through the solution to prevent oxidation. The ion-exchanged crystal was then washed thoroughly in distilled water and placed in a thin-walled capillary connected to a vacuum system, where it was heated to 400° over a 2-hr period. It was held at this temperature for 2.5 hr in air followed by 16 hr at $<10^{-6}$ Torr. After cooling to room temperature, an ampoule of 1-chlorobutane previously placed in the system was broken and the system was allowed to equilibrate for 31 days. The capillary was then sealed with a small torch.

The experimental procedure used in determining the space group (Fd3m) and in collecting and treating the data was very similar to that for *m*-dichlorobenzene–nickel faujasite.[1] A total of 5223 intensities was collected and a reflection was considered statistically observed if $\overline{\Delta I/I}$ was less than 0.75 and if the weighted-average amplitude, $\overline{|F|}$, was greater than three times the weighted-average estimated standard deviation, $\bar{\sigma}$. Absorption corrections were neglected in the present case because of the difficulty in approximating the shape of the crystal and because of the relatively small linear absorption coefficient ($\mu \approx 80\ cm^{-1}$ for Cu Kα radiation). The resultant maximum relative error in the intensities is estimated to be about 25%. The number of averaged independent amplitudes retained was 445.

Refinement of the Zeolite Framework and the Partially Ordered Nonframework Species

Beginning with the final parameters obtained for the located atoms in *m*-dichlorobenzene–nickel faujasite, a series of refinements similar to the series used for the located atoms in that complex ultimately resulted in $R = 0.21$ and $wR = 0.12$. The refinements indicated that the occupancy of these sites is nearly the same as for the corresponding sites in *m*-dichlorobenzene–nickel faujasite if it is assumed that manganese is the occupant of sites I′ and II and that water occupies site II′.

Because of the high *R* obtained with the above refinements, a similar series of refinements was conducted using only the 253 largest amplitudes ($\overline{|F_o|} > 150$). The final *R* values were $R = 0.12$ and $wR = 0.09$, indicating that the counting errors were substantial for reflections having $\overline{|F_o|} < 150$. The final parameters obtained with this series of refinements did not differ from those obtained with the refinements using 445 reflections by more than one estimated standard deviation.

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[1] H. D. Simpson and H. Steinfink, *J. Am. Chem. Soc.*, **91**, 6225 (1969).