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 $\approx$ 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 $\Delta I/I$ 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).

A difference Fourier synthesis calculated using the 253 largest amplitudes showed no significant residual electron density. The largest peaks above background represented about 0.3 e/Å^3. A subsequent Fourier synthesis showed some anisotropy in the Mn2 electron density toward the center of the nearest hexagonal prisms. No anisotropy was evident for any other atom in the structure, however, and the use of anisotropic thermal parameters was not attempted. Interestingly, the Fourier synthesis also showed that the OW3 electron density was very diffuse, in line with a high thermal parameter obtained for this species in the refinements ($B \approx 17$ Å^2). A series of least-squares refinements conducted omitting this electron density, however, gave the values $R = 0.22$ and $wR = 0.15$, significantly higher than the values obtained with OW3 in the model.

The absence of detectable electron density in the supercages suggested that the sorbed 1-chlorobutane molecules and the Mn^{2+} ions unaccounted for at this stage were probably uniformly distributed in the structure. However, the discrepancies between $|F_o|$ and $|F_c|$ for the low-order reflections were not nearly so pronounced as they had been for *m*-dichlorobenzene–nickel faujasite at a similar stage of refinement. A bond angle calculation gave 140 ± 2° for the average (Si,Al)–O–(Si,Al) angle of the present structure, about halfway between the corresponding values for hydrated natural faujasite (142°)[2] and dehydrated nickel(II) faujasite (138°),[3] but not differing from either within experimental error.

Development of the Uniform Distribution Model

In this discussion R_{16} denotes the value of R for the 16 low-order reflections in Table I. The data in the table are from the refinements described above ($R_{16} = 0.087$).

Table I. Low-Order Structure Factor Data for 1-Chlorobutane–Manganese Faujasite[a]

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$	$(\lvert F_o\rvert - \lvert F_c\rvert)$
220	316	396	−80
222	183	−156	27
311	280	320	−39
331	593	−643	−50
333	214	211	3
400	102	−247	−145
440	791	−753	38
444	263	−305	−42
511	482	483	−1
533	1004	−1012	−8
551	274	230	44
555	1495	−1431	64
620	311	298	13
622	107	−114	−7
642	585	−579	6
660	566	656	−90

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

About 17 Mn atoms were accounted for in the previously described refinements on the assumption that only Mn occupies sites I′ and II. This leaves about 11.5 Mn atoms uniformly distributed in the structure. No estimate was available on the number of 1-chlorobutane molecules sorbed in the cavities, but density considerations indicate that a maximum of five to six molecules could exist in 1000 Å^3, the approximate free volume of a supercage.

In view of the results obtained with *m*-dichlorobenzene–nickel faujasite, only uniform distribution models which treated the sorbed 1-chlorobutane molecules as individual carbon, chlorine, and hydrogen atoms were tried in the present analysis. On this basis, structure factors were calculated for models in which two, three, four, and five molecules of 1-chlorobutane were distributed uniformly throughout spheres of 5.5, 6.0, and 6.5 Å in the supercages and in which the 11.5 Mn atoms were distributed to varying extents between these spheres and spheres of 2.3-Å radius in the sodalite cages. The lowest R_{16} values obtained in these trials ranged from 0.072 to 0.078 and were for models which postulated that all of the previously unlocated Mn plus two to three molecules of 1-chlorobutane per supercage are distributed entirely in the supercages, with a radius of distribution of about 5.5–6.0 Å. The two to three molecules of 1-chlorobutane per supercage represents about one-half of the maximum loading and would be expected to give rise to an average (Si,Al)–O–(Si,Al) bond angle between those for the dehydrated and fully loaded structures. The angle obtained for the present structure may thus be indicative of partial loading.

To finalize the model, a radius of distribution of 5.8 Å was used for the sphere representing the supercage, since this was the optimum value obtained for *m*-dichlorobenzene–nickel faujasite and since it falls within the range of the best models described above. A structure factor calculation using the final parameters from the refinements described in the previous section, and using three molecules of 1-chlorobutane and 1.44 Mn atoms uniformly distributed throughout a sphere of 5.8-Å radius in each supercage (with $B = 20$ Å^2), resulted in $R = 0.21$ and $wR = 0.11$ for the data set containing 445 reflections. Further refinement of the parameters for the located species gave $R = 0.20$, with no significant change in wR. The standard deviation of an observation of unit weight was 2.30.

A linear hypothesis test[4] based on wR indicated that the inclusion of the 24 additional parameters required to describe the uniformly distributed species was justified at the 0.005 level of significance.

Atomic scattering factors[5] were used in all of the refinements described thus far. 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 temperature-uncorrected scattering factor as given in the International Tables, $\mu = 4\pi \sin\theta/\lambda$, and $R = 5.8$ Å, the radius of distribution. Ionic scattering factors differ from scattering factors 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 model is based. Another series of least-squares refinements was therefore conducted using only the located species and scattering factors for Si^{3+}, Al^0, O^-, and Mn^{2+}, in order to evaluate the assumption of about 50% ionization in fitting the low-order data. These refinements resulted in no significant changes in either R, wR, or any of the parameters. The value of R_{16} was 0.089,

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

(3) D. H. Olson, *J. Phys. Chem.*, **72**, 4366 (1968).

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

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

Table II. Final Parameters for 1-Chlorobutane–Manganese Faujasite[a]

Atom	Wyckoff notation	Occupancy factor	x	y	z	B, Å^2
(Si,Al)	192(i)	1	−0.053 (3)	0.0354 (3)	0.1255 (3)	1.15 (7)
O1	96(h)	1	−0.106 (1)	0.106 (1)	0	2.7 (4)
O2	96(g)	1	−0.002 (1)	−0.002 (1)	0.1444 (6)	1.0 (3)
O3	96(g)	1	0.173 (1)	0.173 (1)	−0.0284 (6)	2.7 (4)
O4	96(g)	1	0.180 (1)	0.180 (1)	0.3217 (7)	2.8 (4)
Mn2	32(e)	0.38 (1)	0.069 (2)	0.069 (2)	0.069 (2)	6.8 (7)
OW3	32(e)	0.85 (4)	0.151 (3)	0.151 (3)	0.151 (3)	17 (3)
Mn4	32(e)	0.16 (1)	0.238 (5)	0.238 (5)	0.238 (5)	8 (2)
C	8(b)	12	$^3/_8$	$^3/_8$	$^3/_8$	20
Cl	8(b)	3	$^3/_8$	$^3/_8$	$^3/_8$	20
H	8(b)	27	$^3/_8$	$^3/_8$	$^3/_8$	20
MnR1	8(b)	1.44	$^3/_8$	$^3/_8$	$^3/_8$	20

[a] The space group is Fd3m with origin at center of symmetry, and $a_0 = 24.37$ (1) Å. The probable unit cell contents are $(Mn)_{28.5}(SiO_2)_{135}(AlO)_{57} \cdot 24C_4H_9Cl$. The numbers in parentheses in the table are estimated standard deviations applicable in the last digit of the corresponding parameters. MnR1 denotes the uniformly distributed Mn in the supercage.

the same as for the refinements conducted with atomic scattering factors, and the values of $(|F_o| - |F_c|)$ for the low-order reflections were essentially the same as obtained previously. Thus the inclusion of the postulated uniformly distributed electron density would still result in a significant improvement in the model.

The final parameters obtained with atomic scattering factors are shown in Table II. The bond distances and angles for the located atoms are presented in Table III. A table of the $|F_o|$ and final F_c values is available from the authors.

Table III. Final Interatomic Distances and Angles for 1-Chlorobutane–Manganese Faujasite[a]

Atom set	Distance, Å	Atom set	Angle, deg
(Si,Al)–O1	1.62 (4)	O1–(Si,Al)–O2	113 (2)
(Si,Al)–O2	1.61 (4)	O1–(Si,Al)–O3	114 (2)
(Si,Al)–O3	1.67 (4)	O1–(Si,Al)–O4	107 (2)
(Si,Al)–O4	1.64 (4)	O2–(Si,Al)–O3	106 (2)
O1–O2	2.70 (5)	O2–(Si,Al)–O4	106 (2)
O1–O3	2.76 (5)	O3–(Si,Al)–O4	111 (2)
O1–O4	2.62 (5)	(Si,Al)–O1–(Si,Al)	138 (2)
O2–O3	2.61 (5)	(Si,Al)–O2–(Si,Al)	142 (2)
O2–O4	2.59 (5)	(Si,Al)–O3–(Si,Al)	137 (2)
O3–O4	2.73 (5)	(Si,Al)–O4–(Si,Al)	139 (2)
Mn2–OW3	2.2 (2)	O3–Mn2–O3	99 (3)
Mn2–O2	3.1 (1)	OW3–Mn2–OW3	47 (5)
Mn2–O3	2.4 (1)	O3–Mn2–OW3	103 (4)
OW3–OW3	1.8 (1)	Mn2–OW3–Mn2	118 (5)
OW3–O2	3.5 (1)	O2–Mn4–O2	105 (7)
Mn4–O2	2.3 (2)		
Mn4–O4	2.9 (2)		

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

Discussion

This complex differs from *m*-dichlorobenzene–nickel faujasite in that only half the available intracystalline volume is filled. Approximately three molecules of 1-chlorobutane and 1.5 manganese ions are uniformly distributed in each supercage. Also the sodalite cages in the nickel faujasite complex contain some uniformly distributed nickel ions while no manganese ions are uniformly distributed in the sodalite cages of this complex. Crystallographic sites in regions I′ and II′ in the sodalite cages of the present complex are partially occupied by manganese ions and water molecules, respectively, but the electron density representing the water molecules is very diffuse as contrasted with the well-defined distribution observed in the nickel faujasite complex and in natural faujasite.

The inclusion of the uniformly distributed species in the present analysis resulted in a significant decrease in R and in wR. The value of $R = 0.20$ obtained for the data set containing 445 reflections is quite high, but the dramatic decrease in R from 0.21 to 0.12 which resulted in the preliminary refinements when only the 253 reflections having $|F_o| > 150$ were considered indicates that this is mostly due to counting errors in the small intensities. All but one of the low-order reflections (400) have $|F_o| > 150$, so that these reflections are among the more reliable in the data set.

Unfortunately, no independent estimate was available to check the calculated extent of loading in the complex. Aside from the uniform distribution model itself, the only other information available for judging the extent of loading is the calculated mean (Si,Al)–O–(Si,Al) angle of 140°. Although the uncertainty in this angle is sizable compared to the difference between the values for the hydrated and dehydrated structures, it suggests that the framework is only partially loaded. The reason for the apparent partial saturation is unknown.

The arrangement of species in the sodalite cage of this structure is basically the same as in hydrated natural faujasite and *m*-dichlorobenzene–nickel faujasite, except for the diffuse OW3 electron density. This may be due to a situation similar to that described by Smith, *et al.*,[6] in which there is an unresolved electronegative bridging species in the center of some of the cages, between the cations occupying the site I′ positions. The bonding between these cations and OW3 would be less effective under such circumstances. However, the water in the II′ positions in *m*-dichlorobenzene–nickel faujasite and hydrated natural faujasite (cation = Ca^{2+}) is not diffuse. A more likely explanation of the difference between the appearance of the site II′ electron density in these complexes and the present one is therefore that the Ca^{2+} has the size to coordinate effectively with both the water oxygens in the site II′ positions and three of the framework oxygens of the nearby hexagonal prism six rings, and that Ni^{2+} has the polarizing power to do so, while Mn^{2+} does not possess

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

the size and polarizing power which will allow this ion to coordinate effectively and simultaneously to both species.

The bond distance Mn4–O2 = 2.3 Å suggests that site II may be partially occupied by both Mn^{2+} and residual water, or that the bonding of Mn^{2+} in this site to the O2's in the adjacent six-ring is weakened by the association of the cation with the sorbed species.

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The Signs of $^1K_{\rm PC}$ and Other Coupling Constants in Phosphorus and Selenium Compounds

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Abstract: The changes in signs of $^1K_{\rm PC}$ and $^2K_{\rm PCH}$ over a wide range of phosphorus compounds, as well as the signs of PH, SeC, and SeCH couplings, are explained by a model which has been successful in accounting for changes in sign of $^1K_{\rm NN'}$ across the periodic table.

It has been found that it is possible to account for the changes in sign across the periodic table of the reduced spin–spin coupling constants, $K_{\rm NN'}$, of directly bonded nuclei by attributing the changes to nuclear spin–electron spin contact contributions, $\mathcal{A}_{\rm N}$ and $\mathcal{A}_{\rm N'}$, each of which is composed of two parts[1]

$$\mathcal{A}_{\rm N} = \mathcal{A}_{\rm N}({\rm s}) + \mathcal{A}_{\rm N}(\text{core pol})$$

$\mathcal{A}_{\rm N}$(s) is the direct Fermi contact term caused by the s density of the bonding electrons at the nucleus and $\mathcal{A}_{\rm N}$(core pol) is an indirect Fermi contact interaction due to polarization of the s electrons in the core. For an s orbital there is evidence that the core polarization term is positive while for atomic orbitals with nodes at the nucleus the core polarization term is usually negative.[1,2] If the atom employs ns orbitals in the bond, the direct interaction term, $\mathcal{A}_{\rm N}$(s), which is positive, dominates. The bonding of group VII and, to a lesser degree, group VI atoms employs primarily p orbitals. In such atoms the model predicts that the dominant nuclear spin–electron spin interaction is the indirect one, $\mathcal{A}_{\rm N}$(core pol), and probably negative. While both mechanisms $\mathcal{A}_{\rm N}$(s) and $\mathcal{A}_{\rm N}$(core pol) would be in operation in every case, the sign of the coupling constant is determined by the dominant nuclear spin–electron spin interactions for N and N′, since

$$K_{\rm NN'} \propto \mathcal{A}_{\rm N}\mathcal{A}_{\rm N'}$$

It was stated previously that the borderline region where the dominant term is expected to change is in groups V and VI.[1] If the model is valid, we should expect that there should be related but different compounds containing atoms in groups V and VI in which $^1K_{\rm NN'}$ changes sign for a given pair of nuclei N and N′, where N belongs to group V or VI. In agreement with the model proposed in ref 1, hereafter referred to as I, both positive and negative coupling constants are observed for ^{31}P–^{13}C coupling. While the model has been successful in explaining the changes in sign across the periodic table, the transition in sign of the coupling constant between any two given nuclei should likewise be consistently explained by the model. We show that this can be done in compounds of P and Se in agreement with intuitive arguments based on hybridization and the effect of ligand electronegativity on hybridization.

The coupling for which the changing sign over a variety of compounds has been observed is ^{31}P–^{13}C. The ^{77}Se couplings are included in this discussion as a representative of group VI since it is the only one of group VI in which signs of coupling constants have been determined in an extensive number of compounds. The signs and magnitudes of these coupling constants are shown in Tables I and II. Values of $^2K_{\rm PCH}$ and $^2K_{\rm SeCH}$, as well as $^1K_{\rm PH}$ and $^1K_{\rm SeH}$ in the same and related compounds, are included. It is noted that for P(III) compounds, the P–C coupling constant is small negative, becoming positive in P^+(IV) compounds and P(V) compounds, and increasingly positive as more electronegative atoms are bonded to P. At the same time, the geminal PCH coupling is positive for P(III) compounds, becoming negative in P^+(IV) and P (V) compounds. It might be useful to point out that HCH and CCH couplings in saturated systems are negative. The PH coupling is small positive for P(III) compounds, increasing to more than threefold in P(V) compounds. $^1K_{\rm SeC}$ is

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[1] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, in press.

[2] Unrestricted Hartree–Fock calculations of s hyperfine interactions in 3d ions and atoms show that the electron with spin parallel to that of the net spin (3d) is attracted into the 3d region, the regions outside (including the nucleus at $r = 0$) having opposite spin: R. E. Watson and A. J. Freeman, "Hyperfine Interactions," A. J. Freeman and R. B. Frankel, Ed., Academic Press, New York, N. Y., 1967. On the other hand, calculations by D. A. Goodings (*Phys. Rev.*, 123, 1706 (1961)) show that polarization due to s electrons gives only positive spin densities at the nucleus. A possible explanation for this is the following. Inner s electrons are attracted into the regions of high probability for the ns electron, and since these regions include the nucleus at $r = 0$, the core polarization by ns electrons leads to positive contributions to $\mathcal{A}_{\rm N}$(core pol).