

Crystal Structures of Dehydrated Fully Mn^{2+} -Exchanged Zeolite X and of Its Ethylene Sorption Complex

Se Bok Jang, Mi Suk Jeong, and Yang Kim*

Department of Chemistry, Pusan National University, Pusan 609-735, Korea

Karl Seff*

Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822

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The crystal structures of dehydrated $\text{Mn}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384}$ ($a = 24.721(5) \text{ \AA}$) and of its ethylene sorption complex $\text{Mn}_{46}\text{Si}_{100}\text{Al}_{92}\text{O}_{384} \cdot 30\text{C}_2\text{H}_4$ ($a = 24.690(5) \text{ \AA}$) have been determined by single-crystal X-ray diffraction techniques in the cubic space group $Fd\bar{3}$ at $21(1)^\circ\text{C}$. Each crystal was prepared by dehydration at 380°C and 2×10^{-6} Torr for 2 days; the complex was then prepared by exposure to 300 Torr of ethylene gas at $24(1)^\circ\text{C}$, and its structure was determined in this atmosphere. Their structures were refined to the final error indices, $R_1 = 0.050$ and $R_2 = 0.044$ with 316 reflections and $R_1 = 0.064$ and $R_2 = 0.061$ with 313 reflections, respectively, for which $I > 3\sigma(I)$. In each structure, 16 Mn^{2+} ions, each octahedrally coordinated by six oxygens of the zeolite framework, fill site I at the centers of the double six-rings. The remaining 30 Mn^{2+} ions in each structure are at site II in the supercage. Each site-II Mn^{2+} ion in the empty structure is three-coordinate and is quite close to the plane of the three oxygens to which it binds, projecting only 0.14 \AA into the supercage. To coordinate laterally to an ethylene molecule, each moves 0.24 \AA deeper into the supercage. These Mn^{2+} ions are $2.119(11) \text{ \AA}$ from three framework oxygens and $2.76(6) \text{ \AA}$ from each carbon atom of an ethylene molecule ($\text{C}=\text{C} = 1.10(8) \text{ \AA}$). The long Mn^{2+} –ethylene distance is indicative of physisorption.

Introduction

Several hydrocarbon sorption structures of transition metal ion exchanged zeolite A have been reported. In dehydrated $\text{Co}_4\text{Na}_4\text{-A}^1$ and $\text{Mn}_4\text{Na}_4\text{-A}^2$, the transition-metal ions select positions close the anionic zeolite framework where they achieve near-trigonal planar coordination. Upon treating dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ with ethylene³ or acetylene,⁴ or $\text{Mn}_4\text{Na}_4\text{-A}$ with acetylene,^{4,5} four organic molecules are sorbed per unit cell. Each transition-metal ion lies on a 3-fold axis in the large cavity of the unit cell, close to three equivalent trigonally arranged zeolite oxygen atoms and symmetrically close to both carbon atoms of an organic molecule. In the crystal structure of an ethylene sorption complex of partially decomposed and fully Ag^+ -exchanged zeolite A,⁶ ca. 3.6 Ag^+ ions per unit cell are recessed approximately 1.1 \AA into the large cavity where each forms a lateral complex with an ethylene molecule. These Ag^+ ions have a near-tetrahedral environment (counting ethylene as monodentate), $2.49(1) \text{ \AA}$ from three framework oxygens and $2.54(8) \text{ \AA}$ from each carbon atom of an ethylene molecule ($\text{C}-\text{C} = 1.19(12) \text{ \AA}$).

Carter et al. studied the sorption of ethylene at room temperature onto a series of transition metal ion exchanged synthetic near-faujasites by infrared spectroscopy and by microcalorimetry.⁷ They found that C_2H_4 molecules form laterally held complexes of symmetry C_2 . Of the transition-metal ions examined (Ag^+ , Cd^{2+} , Li^+ , Na^+ , K^+ , Ba^{2+} , and Ca^{2+}), Ag^+ and Cd^{2+} were found to hold C_2H_4 most strongly; furthermore, the sorbed ethylene molecules are reported to be rotating freely in all the cases, except in their complexes with Ag^+ and Cd^{2+} . These results are entirely consistent with the crystallographic results above and with those herein reported.

In the crystal structure of an ethylene sorption complex of anhydrous fully Cd^{2+} -exchanged zeolite X,⁸ about 29.5 Cd^{2+} ions are found ($\text{Cd}-\text{O} = 2.221(6) \text{ \AA}$) at site II. Each of these site-II Cd^{2+} ions is recessed $0.50(1) \text{ \AA}$ into the supercage from the plane of the three oxygens to which it is bound. To complete its distorted tetrahedral coordination, each coordinates laterally (symmetrically) to an ethylene molecule (counted as monodentate) in the supercage ($\text{Cd}-\text{C} = 2.70(4) \text{ \AA}$ and $\text{C}=\text{C} = 1.26(5) \text{ \AA}$). The recently completed ethylene complex of $\text{Ca}_4\text{-X}$ is very similar.⁹

To observe the sorption of olefins onto transition metal ion exchanged zeolite X, the structures of dehydrated fully Mn^{2+} -exchanged zeolite X and of its ethylene sorption complex have been determined by single-crystal X-ray diffraction techniques.

Experimental Section

Large single crystals of sodium zeolite X, stoichiometry $\text{Na}_{92}\text{-Si}_{100}\text{Al}_{92}\text{O}_{384}$ exclusive of water molecules, were prepared in St. Petersburg, Russia.¹⁰ Each of two single crystals, colorless octahedra about 0.2 mm in cross section, was lodged in a fine Pyrex capillary.

To prepare fully Mn^{2+} -exchanged zeolite X, a 0.05 M solution of $\text{Mn}(\text{NO}_3)_2$ was used. It was allowed to flow past each crystal at a velocity of approximately 15 mm/s for 5 days at $24(1)^\circ\text{C}$. After dehydration at 380°C and 2×10^{-6} Torr for 2 days, each crystal was red. To prepare the ethylene complex, crystal 2 was treated with 300 Torr of zeolitically dried ethylene for 1 h at $24(1)^\circ\text{C}$. It was then sealed in its capillary in this atmosphere, after which it was observed to be black.

The cubic space group $Fd\bar{3}$ was used throughout this work. This choice is supported by (a) the low Si/Al ratio, which in turn requires, at least in the short range, alternation of Si and Al, and (b) the observation that this crystal, like all other crystals from the same batch, does not have intensity symmetry across

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TABLE 1: ^aPositional, Thermal, and Occupancy Parameters

Crystal 1. Dehydrated Mn ₄₆ -X												
atom	Wyc. pos.	site	x	y	z	U ₁₁ ^b	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	occupancy ^c varied fixed
Si	96(g)		-528(2)	1219(2)	352(2)	230(21)	124(20)	193(22)	-1(22)	-11(20)	24(25)	96
Al	96(g)		-535(2)	367(2)	1215(2)	111(19)	111(21)	99(20)	-24(20)	3(21)	-53(24)	96
O(1)	96(g)		-1078(4)	7(4)	1069(4)	348(67)	277(58)	218(61)	-22(62)	77(44)	-108(58)	96
O(2)	96(g)		-20(4)	-14(4)	1480(3)	31(42)	247(48)	260(50)	115(48)	78(49)	20(54)	96
O(3)	96(g)		-310(3)	622(3)	608(4)	151(49)	0(46)	251(47)	-19(47)	7(52)	-29(42)	96
O(4)	96(g)		-627(4)	832(4)	1683(4)	296(60)	115(52)	220(56)	-43(55)	83(58)	-44(46)	96
Mn(1)	16(c)	I	0	0	0	146(13)	146(13)	146(13)	22(18)	22(18)	22(18)	16.4(2) 16
Mn(2)	32(e)	II	2204(1)	2204(1)	2204(1)	281(11)	281(11)	281(11)	207(14)	207(14)	207(14)	31.5(3) 30
Crystal 2. Ethylene Sorption Complex of Mn ₄₆ -X												
atom	Wyc. pos.	site	x	y	z	U ₁₁ ^b or U _{iso}	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃	occupancy ^c varied fixed
Si	96(g)		-525(2)	1220(3)	350(2)	126(26)	131(26)	134(28)	13(31)	-16(26)	-4(33)	96
Al	96(g)		-534(2)	366(2)	1212(3)	120(27)	99(29)	91(29)	25(27)	-1(31)	-2(34)	96
O(1)	96(g)		-1088(5)	9(7)	1066(5)	313(98)	392(94)	274(90)	-65(86)	-5(64)	-56(84)	96
O(2)	96(g)		-16(5)	-16(5)	1481(4)	39(59)	68(60)	261(69)	33(61)	16(65)	-16(66)	96
O(3)	96(g)		-307(4)	638(5)	609(5)	95(69)	123(71)	236(75)	44(68)	39(70)	-103(63)	96
O(4)	96(g)		-636(5)	823(5)	1695(6)	247(79)	155(73)	216(77)	-158(75)	118(78)	-55(64)	96
Mn(1)	16(c)	I	0	0	0	145(18)	145(18)	145(18)	-4(23)	-4(23)	-4(23)	16.3(2) 16
Mn(2)	32(e)	II	2259(2)	2259(2)	2259(2)	356(17)	356(17)	356(17)	140(22)	140(22)	140(22)	28.5(4) 30
C	96(g)		3092(23)	2747(23)	2820(26)	1238(246) ^d						74(3) 60

^a Positional and anisotropic thermal parameters are given $\times 10^4$. Numbers in parentheses are the esd's in units of the least significant digit given for the corresponding parameter. ^b The anisotropic temperature factor = $\exp[-2\pi^2 a^{-2}(h^2 U_{11} + k^2 U_{22} + l^2 U_{33} + 2hkU_{12} + 2hlU_{13} + 2klU_{23})]$. ^c Occupancy factors are given as the number of atoms or ions per unit cell. ^d $U_{\text{iso}} = (B_{\text{iso}}/8\pi^2)$.

(110) and therefore lacks that mirror plane. Diffraction data were collected with an automated Enraf-Nonius four-circle computer-controlled CAD-4 diffractometer equipped with a pulse-height analyzer and graphite monochromator, using Mo radiation ($K\alpha_1$, $\lambda = 0.709$ 30; $K\alpha_2$, $\lambda = 0.713$ 59 Å). The unit cell constants at 21(1) °C, determined by least-squares refinement of 25 intense reflections for which $14^\circ < 2\theta < 24^\circ$, are $a = 24.721(5)$ Å for crystal 1 and $a = 24.690(5)$ Å for crystal 2, respectively. The intensities of all lattice points for which $2\theta < 60^\circ$ were recorded. Of the 1368 reflections observed for each crystal, only the 316 and 313 unique reflections, respectively, for crystals 1 and 2, for which $I > 3\sigma(I)$ were used in subsequent structure determination. An absorption correction ($\mu = 1.39$ mm⁻¹, $\rho_{\text{cal}} = 1.275$ g/cm³, and $F(000) = 6772$ for Mn₄₆-X; $\mu = 1.40$ mm⁻¹, $\rho_{\text{cal}} = 1.373$ g/cm³, and $F(000) = 7132$ for Mn₄₆-X·30C₂H₄) was made empirically using a Ψ scan for each crystal.¹¹ The adjusted calculated transmission coefficients ranged from 0.995 to 0.999 for Mn₄₆-X and from 0.990 and 0.997 for Mn₄₆-X·30C₂H₄, respectively. These corrections had little effect on the final R indices. Other details are the same as previously reported.^{9,12}

Structure Determination

(a) **Dehydrated Mn₄₆-X.** Full-matrix least-squares refinement of dehydrated Mn₄₆-X was initiated with the atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3), and O(4)] in dehydrated Ca₄₆-X.¹³ Anisotropic refinement of the framework atoms converged to an R_1 index ($\sum |F_o - F_c| / \sum F_o$) of 0.35 and weighted R_2 index ($\sum w(F_o - F_c)^2 / \sum wF_o^2$)^{1/2} of 0.39.

The initial difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.222, 0.222, 0.222) with heights of 8.8 and 8.2 e Å⁻³, respectively. Anisotropic refinement including those at Mn(1) and Mn(2), respectively, converged to $R_1 = 0.050$ and $R_2 = 0.042$. Occupancy refinement converged at 16.4(2) and 31.5(3), respectively. These values were reset and fixed at 16.0 and 30.0 Mn²⁺ ions at Mn(1) and

Mn(2), respectively, because no more than 16 ions may occupy the Mn(1) site and because the cationic charge should be 92+ per $Fd\bar{3}$ unit cell.¹⁰ Full anisotropic refinement converged to $R_1 = 0.050$ and $R_2 = 0.044$ (see Table 1).

In the final cycle of least-squares, all shifts in atomic parameters were less than 0.01% of their corresponding standard deviations. The final difference function was featureless except for a peak of height 0.55 e Å⁻³ at (0.168, 0.082, 0.668). This peak was not within bonding distance of any other atom and was not considered further.

(b) **Mn₄₆-X·30C₂H₄.** Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms of the previous structure, Mn₄₆-X. Anisotropic refinement converged to $R_1 = 0.33$ and $R_2 = 0.36$.

The two largest peaks on a difference Fourier function showed the positions of Mn²⁺ ions at Mn(1) (0.0, 0.0, 0.0) with peak height 10.0 e Å⁻³ and Mn(2) (0.225, 0.225, 0.225) with peak height 6.5 e Å⁻³. Anisotropic refinement of framework atoms and isotropic refinement of Mn(1) and Mn(2) converged to $R_1 = 0.084$ and $R_2 = 0.098$ with occupancies of 16.6(5) and 29.7(7), respectively (see Table 1).

The next difference Fourier function showed the carbon atoms of the ethylene molecules to be at the 96-fold position (0.297, 0.278, 0.276) with a peak height of 1.3 e Å⁻³. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement for all atoms except C, which was refined isotropically, converged to the error indexes $R_1 = 0.064$ and $R_2 = 0.059$. It is assumed that one C₂H₄ molecule is associated with each Mn(2) ion, such coordination being the reason that each Mn(2) ion moved 0.24 Å further into the supercell as compared to the dehydrated structure. Refinement of about 60 carbon atoms per unit cell at this position, constrained to be no more than twice the number of Mn²⁺ ions at Mn(2), converged readily. The occupancies at Mn(1), Mn(2), and C were reset and fixed as in the last column of Table 1. The final error indices converged to $R_1 = 0.064$ and $R_2 = 0.061$. All shifts in the final cycles of least-squares refinement were less than 0.01%

TABLE 2: Selected Interatomic Distances (Å) and Angles (deg)^a

	Mn ₄₆ -X	Mn ₄₆ -X·30C ₂ H ₄
Si-O(1)	1.640(10)	1.636(15)
Si-O(2)	1.698(11) ^b	1.677(14) ^b
Si-O(3)	1.695(9) ^b	1.662(14) ^b
Si-O(4)	1.618(10)	1.616(14)
mean	1.663	1.648
Al-O(1)	1.651(10)	1.666(15)
Al-O(2)	1.712(11) ^b	1.723(14) ^b
Al-O(3)	1.718(10) ^b	1.727(14) ^b
Al-O(4)	1.648(10)	1.660(15)
mean	1.682	1.694
Mn(1)-O(3)	2.282(9)	2.306(13)
Mn(2)-O(2)	2.098(9)	2.119(11)
Mn(2)-C		2.76(6)
C-C		1.10(8)
O(1)-Si-O(2)	113.5(5)	113.4(8)
O(1)-Si-O(3)	106.1(5)	107.6(7)
O(1)-Si-O(4)	114.0(5)	112.1(7)
O(2)-Si-O(3)	107.2(5)	107.3(6)
O(2)-Si-O(4)	103.7(5)	103.4(7)
O(3)-Si-O(4)	112.4(5)	113.1(7)
O(1)-Al-O(2)	113.1(6)	113.8(8)
O(1)-Al-O(3)	105.7(5)	106.6(7)
O(1)-Al-O(4)	114.6(5)	113.0(7)
O(2)-Al-O(3)	107.2(5)	107.6(6)
O(2)-Al-O(4)	102.6(5)	102.0(7)
O(3)-Al-O(4)	113.7(5)	113.8(7)
Si-O(1)-Al	129.9(6)	128.8(9)
Si-O(2)-Al	131.9(6)	131.4(7)
Si-O(3)-Al	122.9(5)	124.2(7)
Si-O(4)-Al	163.3(7)	161.4(9)
O(3)-Mn(1)-O(3)	89.8(3), 90.2(3), 180 ^c	89.6(4), 90.4(4), 180 ^c
O(2)-Mn(2)-O(2)	119.6(4)	116.9(5)
C-Mn(2)-C		23(2)
Mn(2)-C-C		78(4)

^a Numbers in parentheses are estimated standard deviations in units of the least significant digit given for the corresponding value. ^b Only O(2) and O(3) coordinate to Mn²⁺ ions; accordingly their bonds to Si and Al are seen to be longer than those of O(1) and O(4). ^c Exactly by symmetry.

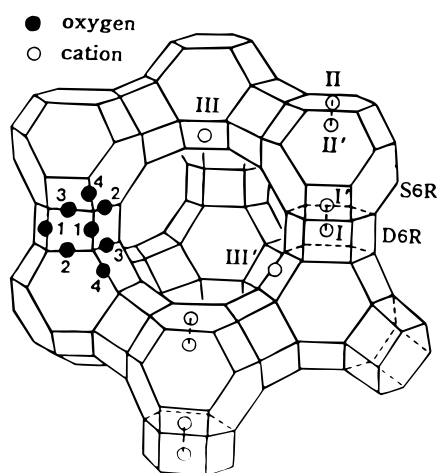


Figure 1. Stylized drawing of the framework structure of zeolite X. Near the center of each line segment is an oxygen atom. The different oxygen positions are indicated by the numbers 1–4. Silicon and aluminum atoms alternate at the tetrahedral intersections, except that Si substitutes for about 4% of the Al's. Extraframework cation positions are labeled with Roman numerals.

of their corresponding standard deviations. The final difference function was featureless except for a peak at (0.235, 0.473, 0.238) of height 0.6 e Å⁻³. This peak was not within bonding distance of any other atom and was not considered further.

Atomic scattering factors^{14,15} for Si, Al, O⁻, C, and Mn²⁺ were used. All scattering factors were modified to account for

TABLE 3: Deviations (Å) of Atoms from the Planes of the O(2) Single Six-Ring Oxygens^a

	Mn ₄₆ -X	Mn ₄₆ -X·30C ₂ H ₄
Mn(2)	0.14(1)	0.38(1)
C		3.06(6)

^a A positive deviation indicates that the atom lies in the supercage.

anomalous dispersion.¹⁶ The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

Zeolite X is a synthetic counterpart of the naturally occurring mineral faujasite (see Figure 1). The 14-hedron with 24 vertices known as the sodalite cavity or β -cage may be viewed as its principal building block. These β -cages are connected tetrahedrally at six-rings by bridging oxygens to give double six-rings (D6Rs, hexagonal prisms) and, concomitantly, an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring (24-membered) windows. The Si and Al atoms occupy the vertices of these polyhedra. The oxygen atoms lie approximately midway between each pair of Si and Al atoms, but are displaced from those points to give near-tetrahedral angles about Si and Al.

The nomenclature of the cation sites is as follows (see Figure 1): site I, at the center of the D6R; site II, at the center of the single six-ring (S6R, shared by a β - and a supercage) or displaced from this point into a supercage; sites I' and II', in the sodalite cavity, on opposite sides of the corresponding six-rings from sites I and II, respectively; and site III, on a 2-fold axis opposite a four-ring inside the supercage.

In the two structures, the mean values of the Si-O and Al-O bond lengths are 1.655 and 1.688 Å, respectively (see Table 2 for further detail). In the crystal structures of the ethylene and acetylene sorption complexes of dehydrated fully Ca²⁺-exchanged zeolite X, these mean values differ more, 1.65 and 1.70 Å, respectively.⁹ In neither case were the acceptable mean Si-O and mean Al-O distances of ca. 1.61 and 1.72 Å, respectively, seen, as they were in dehydrated Mg₄₆-X,¹³ Ca₄₆-X¹³, Ba₄₆-X,¹³ Na₈₈-X,¹⁷ and Cd₄₆-X·28C₂H₂.¹⁸ The individual bond lengths, however, show marked variations: Si-O from 1.616(14) to 1.698(11) Å and Al-O from 1.648(10) and 1.727(14) Å. The longest Al-O and Si-O bonds are to O(2) and O(3), to which the Mn²⁺ ions coordinate; the distortion of the zeolite framework by these small 2+ cations can be seen directly in these values. This distortion is noticeably less than that caused by Cd²⁺, which has a more covalent interaction with the zeolite framework.^{8,18} Olson, Kokotailo, and Charnell noted this in 1968 in calcined Ce³⁺-exchanged faujasite.¹⁹

Only small changes from the framework geometry of the dehydrated structure are observed after ethylene sorption. These are responsible for the slight, commonly observed decrease (about 0.13%) in the cell constant.^{8,9}

In the crystal structure of dehydrated Mn₄₆-X, all Mn²⁺ ions are located at two sites of high occupancy (see Figure 2). Sixteen Mn²⁺ ions at Mn(1) fill the octahedral site I, at the centers of the hexagonal prisms (D6Rs). The octahedral Mn(1)-O(3) distance, 2.282(9) Å, is a little longer than the sum of the ionic radii of Mn²⁺ and O²⁻, 0.80 + 1.32 = 2.12 Å.²⁰ The Mn²⁺ ions at Mn(2) are at site II in the supercage. Thirty of the 32 available positions are occupied. Each Mn²⁺ ion coordinates at 2.098(9) Å to three O(2) framework oxygens and is recessed ca. 0.14 Å into the supercage from the plane of these three O(2)'s. The O(2)-Mn(2)-O(2) bond angle is 119.6(4)°, nearly trigonal planar.

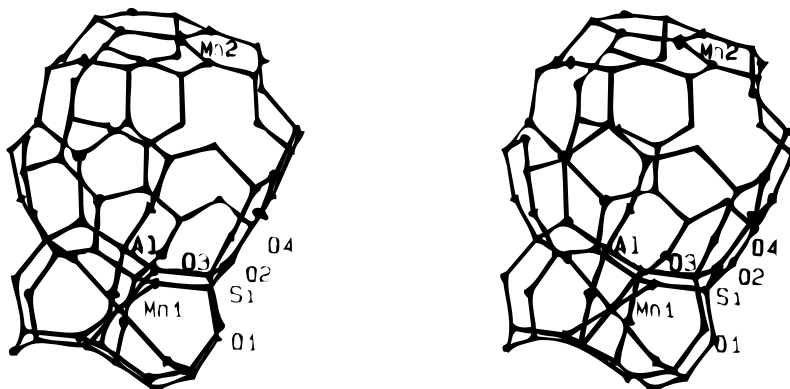


Figure 2. Stereoview of a sodalite cavity with an attached double six-ring (D6R) in dehydrated $\text{Mn}_{46}\text{-X}$. One Mn^{2+} ion at Mn(1) is shown at site I, and four Mn^{2+} ions at Mn(2) are shown at site II. All D6Rs have this arrangement. At least 75% of the sodalite cavities have this arrangement. The remaining 25% have only three Mn^{2+} ions at Mn(2). Ellipsoids of 20% probability are shown.

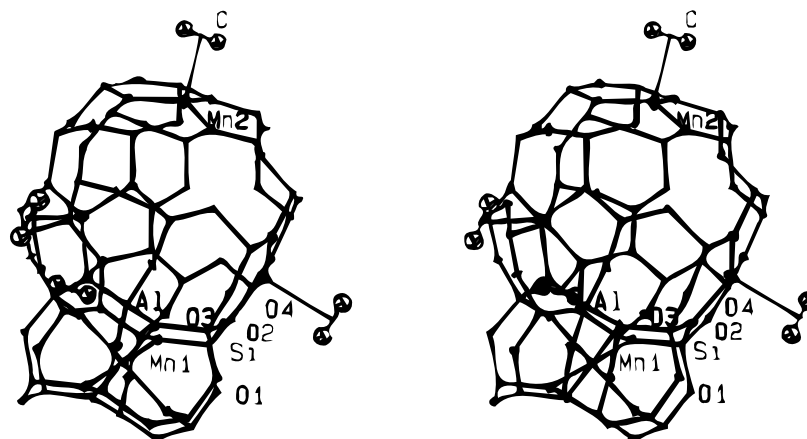


Figure 3. Stereoview of a sodalite cavity with an attached D6R in $\text{Mn}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_4$. One Mn^{2+} ion at Mn(1) is shown at site I, and four Mn^{2+} ions at Mn(2) are shown at site II. All D6Rs have this arrangement. At least 75% of the sodalite cavities have this arrangement. The remaining 25% would have only three Mn^{2+} ions at Mn(2) and only three ethylene molecules. The hydrogen atoms, whose positions were not determined, are not shown. Ellipsoids of 20% probability are shown.

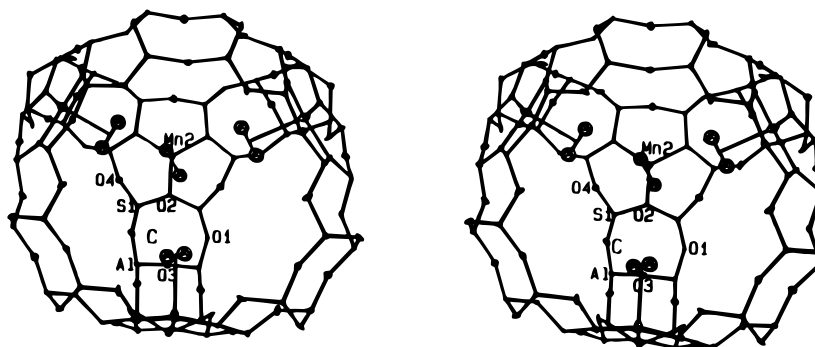


Figure 4. Stereoview of the supercage of $\text{Mn}_{46}\text{-X}\cdot 30\text{C}_2\text{H}_4$. An ethylene molecule is coordinated to each Mn^{2+} ion at Mn(2). The positions of the hydrogen atoms were not determined. As in Figure 3, 25% of the supercages have only three $\text{Mn}(\text{C}_2\text{H}_4)^{2+}$ complexes.

Recently, the crystal structures of fully dehydrated $\text{Ca}_{46}\text{-X}^{13}$ and $\text{Cd}_{46}\text{-X}^{21}$ were determined by single-crystal X-ray diffraction methods. In these structures, all Ca^{2+} and Cd^{2+} cations are located at sites I and II with the same occupancies as $\text{Mn}_{46}\text{-X}$.

To coordinate laterally to ethylene, the Mn^{2+} ions at Mn(2) have moved 0.24 Å further into the supercage (see Table 3), away from their triads of three O(2) oxygens to a more tetrahedral coordination situation (considering ethylene to be monodentate). The O(2)–Mn(2)–O(2) bond angle decreased from a near-trigonal planar value of $119.6(4)^\circ$ in dehydrated $\text{Mn}_{46}\text{-X}$ to $116.9(5)^\circ$ in the ethylene complex. Correspondingly, the Mn(2)–O(2) bond increased slightly from 2.098(9) to 2.119(11) Å. Figures 3, 4, and 5 illustrate the coordination

environment of the Mn^{2+} ions. The Mn²⁺–O bonds increased similarly from 2.11(1) Å in dehydrated $\text{Mn}_{4.5}\text{Na}_3\text{-A}$ to 2.177–(10) Å in its acetylene sorption complex as the O–Mn²⁺–O bond angles decreased from $119.6(1)^\circ$ to $114.9(7)^\circ$.^{4,5}

The Mn(2)–C distance, 2.76(6) Å, is relatively long, indicating that each ethylene molecule binds weakly to Mn^{2+} . The bonding appears to be primarily electrostatic in nature, involving the electric field of the dipositive Mn(II) ions, the polarizable π -electrons of the C_2H_4 molecules, and the positive quadrupole moment of C_2H_4 .²² In the ethylene and acetylene sorption complexes of dehydrated fully Ca^{2+} -exchanged zeolite X,⁹ the Ca^{2+} –C bond distances are longer (Ca^{2+} –C = 2.98(4) Å for the ethylene and 2.87(3) Å for the acetylene sorption complexes). This can be accounted for by the differing ionic radii

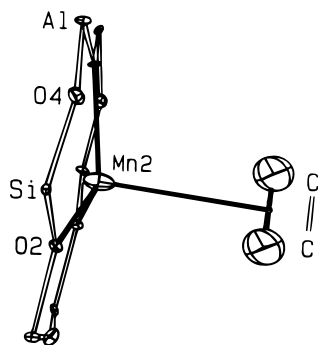


Figure 5. Mn(C₂H₄)²⁺ complex in the supercage. The approximately tetrahedral coordination about Mn²⁺ can be seen. Ellipsoids of 20% probability are used.

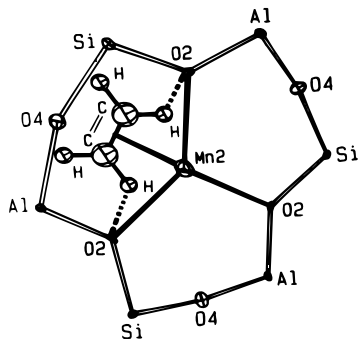


Figure 6. View through a S6R into the supercage showing a Mn²⁺ ion coordinated to an ethylene molecule with hydrogen atoms at calculated positions. Two *cis* hydrogen atoms appear to interact weakly with O(2) oxygens. Ellipsoids of 20% probability are used.

of Mn²⁺ and Ca²⁺, 0.80 and 0.99 Å respectively, so no effect due to the transition-metal nature of Mn²⁺ is seen. The Mn(2)–C bond length herein reported, 2.76(6) Å, agrees well with the Mn–C distances of 2.63(17) Å in Mn_{4.5}Na₃–A·4C₂H₂.^{4,5}

The positions of the four hydrogen atoms of each ethylene molecule were calculated using the software system SHELXL-93.²³ The plane of the ethylene molecule is assumed to be perpendicular to the Mn–(C–C midpoint) line. Two hydrogens are about 2.7 Å from framework oxygens (see Figure 6). This indicates that they may interact weakly with the zeolite

framework oxygens; the sum of the van der Waals radii of oxygen and hydrogen is 1.4 + 1.2 = 2.6 Å.²⁴ This interaction may be responsible for the displacement of each ethylene molecular axis from a unit-cell 3-fold axis; the center of a C=C bond is about 0.32 Å from a 3-fold axis.

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Supporting Information Available: Tables of calculated and observed structure factors (10 pages). Ordering information is given on any current masthead page.

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