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The Crystal Structure of Vacuum-Dehyrated Fully Ammonium-Exchanged Zeolite A

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Abstract: The crystal structure of fully ammonium-exchanged zeolite A dehydrated at 25 °C and 10^{-5} torr has been determined by single-crystal X-ray diffraction techniques in the space group *Fm*3*c* ($a = 24.568$ (2) Å). The structure was refined to a final *R* (weighted) index of 0.040. The NH_4^+ ions are distributed over four sites. Occupancies refine to give 69.4 per unit cell associated with 6-oxygen rings of the aluminosilicate framework (25.8 recessed 1.80 Å into the sodalite units and 43.6 extending 1.43 Å into the large cavities), 21.6 associated with 8-oxygen rings, and 4.0 opposite 4-oxygen rings. The shortest N–O distances for the four NH_4^+ ion positions are 2.99, 2.79, 2.93, and 3.16 Å, respectively. A model with stoichiometric occupancies (24, 44, 24, and 4 ammonium ions per unit cell at the sodalite-unit threefold-axis, the large-cavity threefold-axis, the 8-oxygen-ring, and the 4-oxygen-ring sites, respectively) is proposed. Since there are only 64 6-oxygen rings per unit cell to accommodate the 24 + 44 = 68 threefold axis cations, four (5.4 if refined occupancies are used) must have two NH_4^+ ions associated with them. This appears to be one of two relatively unsatisfactory sites adopted by the eight cations per unit cell that cannot be accommodated by the 64 6-oxygen-ring and the 24 8-oxygen-ring sites. The second is that opposite a 4-oxygen ring. At this position an NH_4^+ ion can hydrogen bond to only two framework oxygens, and those hydrogen bonds are far from linear. Refinement in the space group *Fm*3*c*, which takes account of the Si and Al ordering, did not allow hydrogen positions to be located as hoped, but the inclusion of calculated hydrogen positions lowered *R* values and allowed the otherwise obscure 4-oxygen-ring NH_4^+ position to be found. Of the 107 observed *b* reflections, 30 are inconsistent with the *c* glide condition of *Fm*3*c*. Apparently the NH_4^+ ions are not completely disordered in one or more of their *Fm*3*c* equipoints; that ordering results in violations of the *c* glide symmetry.

The H^+ form of zeolite A, H_{12}-A,[1] is not crystalline because too many Si–O–Al linkages in the aluminosilicate lattice are disrupted.[2] However, there is evidence that the framework can be reconstituted.[3] Upon exposure to hydrogen gas, a Ag_{12}-A crystal lost its diffraction pattern, apparently because silver metal migrated out of the zeolite leaving protons inside. Subsequent heating of this crystal in an oxygen atmosphere caused most of the silver atoms to be reabsorbed and the single-crystal diffraction pattern to be fully restored.

If H_{12}-A could be prepared by an alternate route, then metals other than silver might be used to reconstitute the zeolite; this could be a new method for introducing ions into zeolite A. One relatively gentle, nonaqueous approach to making H_{12}-A in the absence of Ag is via the deammination of $(NH_4)_{12}$-A.

Although the structure of H_{12}-A is not amenable to crystallographic analysis, that of its precursor and perhaps that of its daughter (after metal sorption) are. The determination of the crystal structure of hydrated $(NH_4)_{12}$-A was expected to be a formidable problem (primarily because nitrogen and oxygen would be virtually indistinguishable) and to be relatively uninformative, but the structure of the dehydrated material could be interesting.

Because evacuation of Cd_6-A at 25 °C removes all but five and one half nonframework oxides (four coordinated to Cd^{2+} ions as OH^- or H_2O and one and one half associated with 8-ring oxides as H_3O^+) per 12.24-Å pseudocell[4] and because the bond between H_2O and NH_4^+ was expected to be far weaker, it was anticipated that a similar evacuation of $(NH_4)_{12}$-A might result in complete dehydration. (An ammonium ion can only hydrogen bond to water molecules; it cannot form a coordinate bond to them as can metal cations.) Evacuation under such mild conditions was not expected to threaten the integrity of the NH_4^+ ions.

The zeolite A framework can accommodate 11 cations relatively well at eight 6-ring and three 8-ring sites in each pseudocell, but that is one short of the 12 sites needed by monopositive cations to balance the 12– anionic charge. Consequently, the twelfth ion must occupy a somewhat less satisfactory position in the structure. In anhydrous Na_{12}-A this cation position is located in the large cavity opposite a 4-ring.[5] A similar position is observed for a Tl^+ ion in Cs_9Tl_3-A.[6] Since an NH_4^+ ion must associate with framework oxygens via hydrogen bonds, it may be less adaptable than either Na^+ or Tl^+ and therefore may select a different "twelfth-cation" site.

An ammonium-exchanged zeolite A crystal contains no atoms heavier than those of the framework. Furthermore, the NH_4^+ ion is monopositive and relatively large, so the positive charges are arranged in an unusually diffuse manner in space, and local distortions of the zeolite lattice should be minimal. It was expected, therefore, that the framework-atom order would not be obscured as much as it usually is and that the *b* reflections would be particularly numerous and intense, so refinement in the space group *Fm*3*c* (instead of *Pm*3*m* which assumes Si and Al disorder) would be unusually appropriate. If such a refinement were successful and the framework atoms were more accurately described, the location of the hydrogen atoms of NH_4^+ ions might be possible.

To begin an investigation of the dehydration and deammination behavior of $(NH_4)_{12}$-A, so subsequent experiments involving H_{12}-A might be better understood, and to learn how the arrangement of NH_4^+ ions in dehydrated zeolite A compares with those of other monopositive ions, we determined the crystal structure of $(NH_4)_{12}$-A evacuated at 25 °C and 10^{-5} torr.

Experimental Section

Crystals of zeolite A were prepared by Charnell's method.[7] A single crystal, a cube 0.08 mm on an edge, was lodged in a fine-glass capillary. Ion exchange was performed using flow methods: an aqueous, ammoniacal (ca. 1 M NH_4OH, Mallinckrodt, analytical reagent) solution of 1 M NH_4NO_3 (Baker & Adamson, reagent) was allowed to flow past the crystal at a velocity of approximately 5 mm/s for 72 h at 25 °C. The high NH_4^+/H_3O^+ ratio in this solution, 1.8×10^9, should have discouraged H_3O^+ exchange.[8] The crystal was evacuated at 25 °C and 10^{-5} torr for 48 h and then sealed in its capillary, still under vacuum, with a

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[1] A discussion of nomenclature is available: (a) Yanagida, R. Y.; Amaro, A. A.; Seff, K. *J. Phys. Chem.* **1973**, *77*, 805. (b) Broussard, L.; Shoemaker, D. P. *J. Am. Chem. Soc.* **1960**, *82*, 1041. (c) Seff, K. *Acc. Chem. Res.* **1976**, *9*, 121.

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torch. Diffraction intensities were collected on this crystal at 23 (2) °C.

A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used for preliminary experiments and for the collection of diffraction intensities. Initially, molybdenum radiation ($K\alpha_1$, $\lambda = 0.709\,300$ Å; $K\alpha_2$, $\lambda = 0.713\,590$ Å) was used, and data were collected in the cubic space group *Pm*3*m* (no systematic absences) for reasons discussed previously.[9] The cell constant $a = 12.287$ (1) Å was determined by a least-squares treatment of 15 intense reflections for which $19° < 2\theta < 24°$.

Reflections from two intensity equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, $\bar{h}k\bar{l}$, $k \leq l \leq h$) were examined by using the θ–2θ scan technique. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} from 1° (in 2θ) below the calculated $K\alpha_1$ peak to 1° above the $K\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of 3 reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small random fluctuations of these check reflections were noted during the course of data collection. All unique reciprocal lattice points (884) for which $2\theta < 70°$ were examined. The high upper limit for 2θ was chosen to give a more complete data set, even though few reflections with large 2θ values showed significant intensity.

The crystal was then examined in the lower space group *Fm*3*c*[10-12] which recognizes the silicon/aluminum ordering of the zeolite A framework. Molybdenum radiation proved to have too low an intensity to yield many *b* reflection data even with a scan rate of 0.5 deg min^{-1}, so copper radiation ($K\alpha_1$, $\lambda = 1.540\,562$ Å; $K\alpha_2$, $\lambda = 1.544\,390$ Å) was used.

Reflections for the supercell ($a = 24.568$ (2) Å) from four intensity equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, $h\bar{k}\bar{l}$, $h \leq k \leq l$, $\bar{h}\bar{k}\bar{l}$, $l \leq h \leq k$, and $\bar{h}k\bar{l}$, $h \leq k \leq l$) for which $2\theta < 116°$ (567 unique reciprocal lattice points) were examined under the same conditions as before, except that the scan rate was reduced to 0.5 deg min^{-1}. The data collection mode of the diffractometer was then changed from bisecting (ω circle between the incident beam and the detector) to parallel (detector between the incident beam and the ω circle) so that data for some higher 2θ values could be collected. Two intensity equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, $h\bar{k}\bar{l}$, $h \leq k \leq l$) for which $116° < 2\theta < 158°$ (296 unique reciprocal lattice points) were examined in this manner. Of the total 863 reciprocal lattice points examined, 730 were consistent with the space group *Fm*3*c*. The remaining 133 were of the type *hhl* with *h*(*l*) odd.

The raw data for each region were corrected for Lorentz and polarization effects including that due to incident beam monochromatization; for each radiation, the reduced intensities were merged and the resultant esd's were assigned to each averaged reflection by the computer program COMPARE.[13] Other details regarding data reduction have been discussed previously.[14] An absorption correction (μR ca. 0.03 for Mo $K\alpha$ and ca 0.23 for Cu $K\alpha$) was not applied.[15]

Only the 265 reflections in the Mo$K\alpha$ data set for which the net count exceed three times its corresponding esd were used in structure solution and refinement in the space group *Pm*3*m*. In order to include as many of the *b* reflections as possible in the *Fm*3*c* work, we treated all those reflections in the Cu $K\alpha$ data set for which the net count exceed twice its corresponding esd as observed. This amounted to 499 reflections, of which 392 had even-numbered Miller indices and 107 had odd-numbered ones. Of those 107, 30 were inconsistent with the requirements for the space group *Fm*3*c* (Table I).

Since violations of the assumed space group had been found, those reflections which had not been included in data collection because a face-centered unit cell had been assumed were examined, but no reflection with mixed (even and odd) Miller indices showed significant intensity. To ascertain whether or not the unit cell was indeed cubic, the intensity symmetries of several reflections (3,3,5; 3,3,11; 1,5,9) were examined, but only insignificant deviations were found.

Table I. Reflections in Violation of the *c* Glide Condition of the Space Group *Fm*3*c*

h	*k*	*l*	I^a	$\sigma(I)$	*h*	*k*	*l*	*I*	$\sigma(I)$
1	1	5	608	124	5	5	15	160	55
1	1	9	198	74	5	5	17	123	54
1	1	11	212	61	5	5	19	201	50
1	1	13	294	58	5	5	21	97	42
3	3	3	694	128	5	11	11	355	57
3	3	5	1682	125	7	7	7	2115	76
3	3	11	1364	69	7	7	17	179	52
3	3	13	254	57	7	7	27^a	98	44
3	3	17	198	53	7	9	9	150	56
3	3	23	88	39	7	15	15	111	44
3	7	7	486	68	11	11	11	233	54
3	13	13	168	53	11	11	13	125	51
5	5	7	334	70	11	11	19	148	41
5	5	9	174	63	13	13	21^a	82	40
5	5	11	528	62	13	15	15	104	40

[a] For each reflection, the total net intensity count *I* from four equivalent regions of reciprocal space is given, except for 7,7,27 and 13,13,21, the two highest angle reflections, for which only two such regions were examined. See Experimental Section for details. Structure factors and esd's for these 30 reflections are presented in Table S2 of the supplementary material.

Structure Determination

Full-matrix least-squares refinement in the pseudocell (Mo $K\alpha$ data set) was initiated with the atomic coordinates of the framework atoms [(Si,Al), O(1), O(2), and O(3)] in dehydrated Na_{12}-A.[5] This model converged with an R_1 index, $(\sum|F_o - |F_c||)/\sum F_o$, of 0.167 and a weighted R_2 index, $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.197. A difference Fourier function showed two large peaks on the threefold axis. One refined as 3.9 (2) nitrogens in the sodalite unit and the other as 6.7 (2) nitrogens in the large cavity. Addition of these two positions to least-squares refinement lowered the error indices to $R_1 = 0.082$ and $R_2 = 0.080$. A subsequent difference function revealed another peak at $(0, {}^1/_2, {}^1/_2)$, which refined as approximately 3.5 nitrogens with $R_1 = 0.062$ and $R_2 = 0.046$. Anisotropic refinement of this third position, with an occupancy of 3.0 (the maximum for this position), resulted in $U_{11} = 0.3327$ Å^2 and $U_{22} = U_{33} = 0.1461$ Å^2. These relatively large thermal parameters suggested that the nitrogens were near, but not at, the highly symmetric $(0, {}^1/_2, {}^1/_2)$ position, and isotropic refinement of a position with *m* (*x*,*z*,*z*) rather than 4/*mmm* symmetry was successful.

It was reasoned that since the exchange procedure had been exhaustive and since no Na^+ positions were evident, complete ammonium exchange must have been achieved. Furthermore, since NH_4NO_3 is a strong salt, occlusion of excess NH_4NO_3 is unlikely. Therefore the stoichiometric number of 12 NH_4^+ ions per unit cell was assumed. Since the nitrogen in an ammonium ion accounts for only 70% of its total number of electrons, it was considered probable that occupancy refinements on the basis nitrogen alone would be high. Accordingly, the occupancy factors for the two threefold axis positions were rounded down to 3.0 nitrogens per unit cell in the sodalite unit and 6.0 in the large cavity.

Anisotropic refinement of all but the 8-ring nitrogen position, which was refined isotropically, converged with the final error indices $R_1 = 0.059$ and $R_2 = 0.046$. The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 2.12; *m* (265) is the number of observations and *s* (30) is the number of variables in least-squares. All shifts in the final cycle of refinement were less than 2% of their corresponding esd's.

Full-matrix least-squares refinement in the space group *Fm*3*c* (Cu $K\alpha$ data set with the 30 reflections listed in Table I removed) was initiated with the structural parameters of hydrated Na_{12}-A[10] for the framework atoms, and appropriately adjusted parameters for the two threefold axis nitrogen positions found in the pseudocell. This model converged with $R_1 = 0.087$ and $R_2 = 0.101$. It was not obvious in which direction the 8-ring nitrogen position should deviate from the diagonal mirror plane ($y = z$), which is present in *Pm*3*m* but absent in *Fm*3*c*, so its position was not included in

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Table II. Positional, Thermal,[a] and Occupancy Parameters for Dehydrated $(NH_4)_{12}$-A

A. With Refined Nitrogen Occupancies

	Wyckoff position	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy factor[b]
Si	96 (*i*)	0	938 (1)	1855 (2)	15 (2)	18 (2)	13 (2)	0	0	3 (1)	96.0
Al	96 (*i*)	0	1886 (2)	909 (2)	27 (2)	17 (2)	21 (2)	0	0	5 (2)	96.0
O(1)	96 (*i*)	0	1157 (2)	2468 (6)	95 (4)	41 (3)	16 (3)	0	0	4 (6)	96.0
O(2)	96 (*i*)	0	1441 (3)	1468 (4)	32 (2)	20 (6)	26 (6)	0	0	6 (2)	96.0
O(3)	192 (*j*)	533 (3)	581 (3)	1751 (1)	42 (4)	47 (4)	71 (2)	27 (2)	30 (3)	26 (3)	192.0
N(1)	64 (*g*)	533 (4)	533 (4)	533 (4)	61 (8)	61 (8)	61 (8)	20 (6)	20 (6)	20 (6)	25.8 (6)
N(2)	64 (*g*)	1290 (2)	1290 (2)	1290 (2)	35 (3)	35 (3)	35 (3)	7 (2)	7 (2)	7 (2)	43.6 (3)
N(3)	192 (*j*)	177 (10)	2328 (7)	2328 (7)	51 (11)						21.6 (4)
N(4)	96 (*h*)	1295 (24)	1295 (24)	2500[c]	14 (25)						4.0 (4)

	Wyckoff position	x	y	z	U, Å^2	occupancy factor		Wyckoff position	x	y	z	U, Å^2	occupancy factor
H(1A)	192 (*j*)	444	463	924	76	84.0	H(3A)	192 (*j*)	115	1929	2390	76	24.0
H(1B)	64 (*g*)	298	298	298	76	28.0	H(3B)	192 (*j*)	116	2410	1932	76	24.0
H(2A)	192 (*j*)	1046	1065	1526	76	132.0	H(3C)	192 (*j*)	560	2421	2426	76	24.0
H(2B)	64 (*g*)	1525	1525	1525	76	44.0	H(3D)	192 (*j*)	−81	2542	2553	76	24.0

B. With Idealized Nitrogen Occupancies

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	occupancy factor
N(1)	535 (4)	535 (4)	535 (4)	52 (5)	52 (5)	52 (5)	17 (6)	17 (6)	17 (6)	24.0
N(2)	1290 (2)	1290 (2)	1290 (2)	36 (2)	36 (2)	36 (2)	6 (3)	6 (3)	6 (3)	44.0
N(3)	186 (10)	2322 (6)	2322 (6)	69 (12)						24.0
N(4)	1292 (25)	1292 (25)	2500[c]	18 (20)						4.0

[a] Positional parameters are given $\times 10^4$ and thermal parameters $\times 10^3$. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. Those parameters without esd's shown were held fixed in least-squares refinement. See Figure 1 for the identities of the atoms. The anisotropic temperature factor is $\exp[-2\pi^2(h^2(a^*)^2U_{11} + k^2(b^*)^2U_{22} + l^2(c^*)^2U_{33} + 2hk(a^*b^*)U_{12} + 2hl(a^*c^*)U_{13} + 2kl(b^*c^*)U_{23})]$. [b] Occupancy factors are given as the number of atoms or ions per unit cell. [c] Exactly one-fourth by symmetry.

the initial refinement. It was hoped that question could be resolved by examining a difference Fourier function, but the resolution of the peak was not high enough to allow such subtleties to be seen. Refinements with $y > z$ and with $z > y$ for that position were inconclusive. Both refinements converged with very similar R values and with a N(3) position making one short (ca. 2.85 Å) and one long (ca. 3.15 Å) approach to framework O(1) oxygens. The y and z coordinates of a position calculated to be equidistant from the two O(1) oxygens (which seemed to be a more likely arrangement) were nearly equal with y slightly larger than z. These coordinates were so similar that independent least-squares refinement of them would not be possible, yet the position seemed much more sensible than either of the refined ones. Consequently the y and z coordinates of the N(3) position were constrained to be equal.

An occupancy refinement of the three nitrogen positions resulted in 27.0 nitrogens per unit cell at N(1), 53.4 at N(2), and 26.6 at N(3). These were adjusted down as before to 24, 48, and 24 (corresponding to 3.0, 6.0, and 3.0 in the pseudocell), respectively, and were fixed at those values. This model converged with $R_1 = 0.069$ and $R_2 = 0.063$.

It was hoped that refinement in this lower space group which better describes the positions of the framework atoms would allow the H atoms of the ammonium ions to be located. Unfortunately, a difference Fourier function did not reveal distinct peaks but only diffuse regions of electron density in the vicinity of each of the N atoms. All attempts to refine representative positions were unsuccessful.

For each of the threefold axis N atoms, positions for two sets of tetrahedrally placed H atoms (one set oriented toward O(3) framework oxygens and the other toward O(2) oxygens) were calculated. Occupancy refinements for these calculated positions indicated that the hydrogens of all of these ammonium ions were directed toward O(3) oxygens. Rotating the principal NH_4^+ ion (with H's pointing toward O(3) oxygens) 15° about the threefold axis in either direction caused the error indices to increase very slightly and the effected H atom occupancy to decrease. Addition of calculated H positions for all of the ammonium ions to the structure factor calculation reduced the error indices to $R_1 = 0.060$ and $R_2 = 0.053$. At this point, the two lowest angle reflections, 0,0,2 and 0,2,2, were deleted from the data set because of apparent extinction. This caused the R values to decrease to $R_1 = 0.057$ and $R_2 = 0.045$. A difference Fourier function generated by using this model with 96 NH_4^+ ions per unit cell showed a small peak (Figure 1) at 0.125, 0.125, $^1/_4$. Although this position appeared to be an awkard one either for an NH_4^+ ion or for a residual H_2O molecule, it was tried in least-squares refinement. Surprisingly, it refined as approximately 4 nitrogens per unit cell and caused both error indices to decrease by 0.001. Since this model contained 100 nitrogens per unit cell instead of the expected 96 and since no NO_3^- anions were evident, another occupancy refinement (with hydrogens present this time) was done. Hydrogen occupancies were adjusted to correspond more closely to the appropriate N refined ones, and the refinement was repeated. To avoid any bias introduced by the assumption of rational occupancies, this refinement, which resulted in the nitrogen occupancies given in Table IIA and the error indices $R_1 = 0.053$ and $R_2 = 0.040$, is considered the final one. The goodness-of-fit is 3.09, the number of observations 467, and the number of variables 49. All shifts in the final

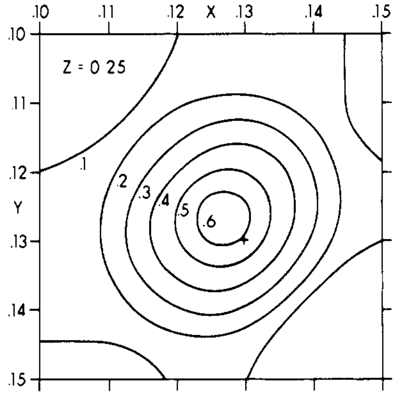

Figure 1. A section through the N(4) peak of an electron-density difference function. Contours at intervals of 0.1 e Å^{-3} are drawn, and the position to which N(4) refined by least-squares is indicated.

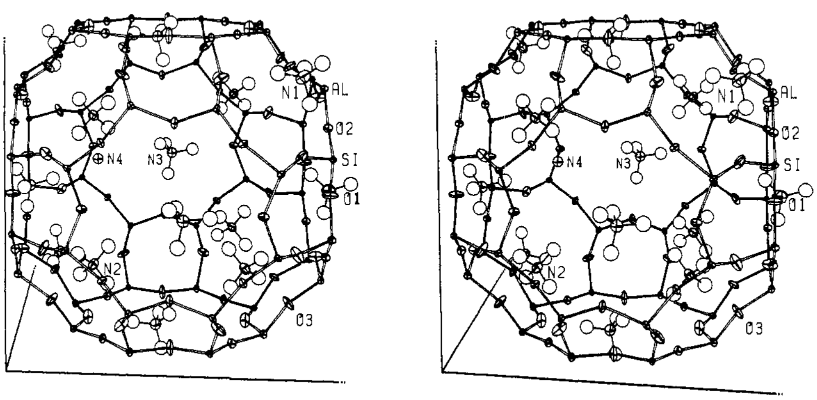

Figure 2. A stereoview[13] of a likely atomic arrangement in a particular large cavity in dehydrated $(NH_4)_{12}$-A. Ellipsoids of 20% probability are shown.

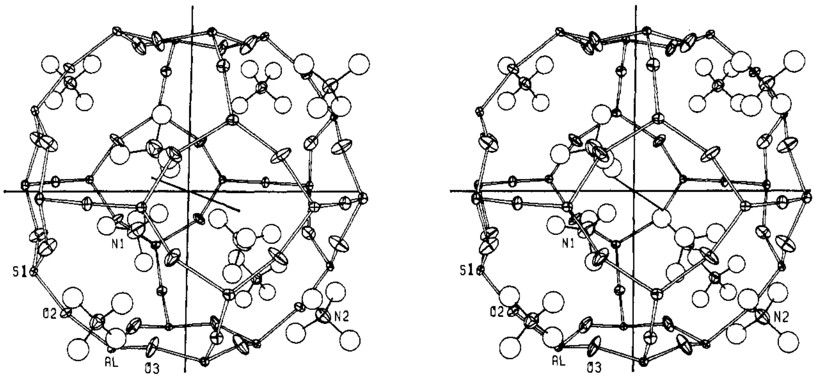

Figure 3. A stereoview[13] of a likely atomic arrangement in a particular sodalite unit in dehydrated $(NH_4)_{12}$-A. Ellipsoids of 20% probability are shown.

cycle of refinement were less than 5% of their corresponding esd's.

Numerous models with rational occupancies for the four nitrogen positions were refined. In all of these refinements, an occupancy of 24.0 nitrogens per unit cell at N(3) was assumed, since the refined value of 21.6 was close to that and since 24 is a sensible number for that position (corresponding to one NH_4^+ ion in each 8-ring of the structure). Raising or lowering the occupancies of N(2) or N(4) (from the idealized values 44.0 and 4.0, respectively) caused relatively high increases in the *R* values regardless of the model used for the rest of the structure. However, decreasing the occupancy at N(1) from 25.8 to 24.0 caused no significant increase, probably because its thermal parameters were able to compensate for the change. This model with 24.0 nitrogens at N(1), 44.0 at N(2), 24.0 at N(3), and 4.0 at N(4) (and with appropriately adjusted hydrogen atom occupancies) converged with the error indices insignificantly different from the refined-occupancy one. The structural parameters for the four nitrogen positions in this refinement are presented in Table IIB.

The largest peak on the final difference Fourier function (generated by using the structural parameters in Table IIA), whose esd is 0.05 e Å^{-3} at a general position, was 1.1 e Å^{-3} in height and was located at $^1/_4$, $^1/_4$, $^1/_4$ where the esd is 0.24 e Å^{-3}.[16] For confirmation that the peak was indeed spurious, the position was tried in least-squares refinement, where it refined to a near-zero occupancy. The Fourier function was otherwise featureless.

The final structural parameters are presented in Table IIA. Interatomic distances and angles are given in Table III. Likely atomic arrangements in a particular large cavity and in a particular sodalite unit are shown in Figures 2 and 3, respectively.

The full-matrix least-squares program[13] used in both structure determinations minimized $\sum w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of σ, its standard deviation. Atomic scattering factors[17,18] for $(Si,Al)^{1.75+}$ [for the *Pm*3*m* structure], Si^{2+}, $Al^{1.5+}$, O^-, N^0, and H^0[19] were used. The functions describing Si^{2+}, $Al^{1.5+}$, and $(Si, Al)^{1.75+}$ are the means, respectively, of the Si^0 and Si^{4+} functions, the Al^0 and Al^{3+} functions, and the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. Scattering factors for all atoms except H were modified to account for the real component (f')

Table III. Selected Interatomic Distances (Å) and Angles (Deg)[a]

Si-O(1)	1.60 (1)	Al-O(1)	1.70 (1)
Si-O(2)	1.56 (1)	Al-O(2)	1.76 (1)
Si-O(3)	1.60 (1)	Al-O(3)	1.73 (1)
N(1)-O(2)	3.46 (1)	N(3)-O(1)	2.93 (2)
N(1)-O(3)	2.99 (1)	N(3)-O(1)	2.95 (2)
N(1)-N(1)	3.70 (3)	N(3)-O(2)	3.07 (2)
N(1)-N(2)	3.22 (3)	N(4)-O(1)	3.20 (6)
N(2)-O(2)	3.221 (4)	N(4)-O(3)	3.16 (7)
N(2)-O(3)	2.789 (5)		
O(1)-Si-O(2)	107.9 (3)	O(2)-Al-O(3)	107.3 (3)
O(1)-Si-O(3)	109.6 (5)	O(3)-Al-O(3)	111.0 (4)
O(2)-Si-O(3)	109.7 (4)	Si-O(1)-Al	139.3 (4)
O(3)-Si-O(3)	110.2 (4)	Si-O(2)-Al	166.1 (4)
O(1)-Al-O(2)	107.5 (4)	Si-O(3)-Al	149.2 (3)
O(1)-Al-O(3)	111.7 (4)		
O(2)-N(1)-O(2)	93.9 (3)	N(1)-H(1A)-O(3)[b]	154
O(3)-N(1)-O(3)	87.7 (4)	N(2)-H(2A)-O(3)[b]	162
O(2)-N(2)-O(2)	103.4 (3)	N(3)-H(3A)-O(1)[b]	177
O(3)-N(2)-O(3)	96.2 (2)	N(3)-H(3B)-O(1)[b]	177
O(1)-N(3)-O(1)	105.0 (8)	H(2B)-N(4)-H(2B)[b]	143
O(1)-N(4)-O(1)	77.8 (5)	N(2)-H(2B)-N(4)[b]	107
O(3)-N(4)-O(3)	71 (2)		

[a] The numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter.
[b] The hydrogen positions were not refined, so angles involving those positions are only approximate.

Table IV. Deviations of Atoms (Å) from the [111] Planes at O(3)[a]

N(1)	-1.80	O(2)	0.06
N(2)	1.43		

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin.

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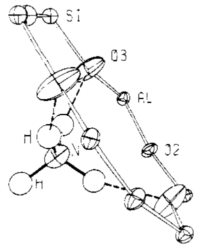

Figure 4. The interaction between an NH_4^+ ion and the O(3) oxygens of a 6-ring. Ellipsoids of 50% probability are shown.

of the anomalous dispersion correction.[20,21]

Discussion

For simplicity, the following discussion will be presented in terms of the 12.284-Å pseudocell, whose volume is one-eighth that of the better *Fm*3*c* unit cell.

The ammonium ions are distributed over four sites (Figure 2). Approximately 3.0 per pseudocell are at N(1), recessed 1.80 Å into the sodalite unit from the [111] planes at O(3) (Table IV), where each hydrogen bonds to three O(3) framework oxygens at 2.99 (1) Å (Table III). Another 5.5 NH_4^+ ions, at N(2), are also located on threefold axes but are on the large-cavity side of the 6-ring planes, and each of these approaches three O(3) oxygens at 2.789 (5) Å. Since the combined occupancy at N(1) and N(3) is 8.5 and since there are only eight 6-rings per pseudocell, one 6-ring in every other pseudocell must have two NH_4^+ ions associated with it. The interaction between an NH_4^+ ion and the O(3) oxygens of a 6-ring is shown in Figure 4. Approximately 3.0 ammonium ions are at N(3) associated with O(1) oxygens of 8-rings. Each N(3) nitrogen makes two nearly linear hydrogen bonds of approximately 2.94 (2) Å to two of these O(1) oxygens. The fourth NH_4^+ ion position, with approximately half of an NH_4^+ ion per pseudocell, is at N(4), opposite a 4-ring of the zeolite framework. Each ammonium ion at this position approaches two O(1) oxygens at 3.20 (6) Å or two O(3) oxygens at 3.16 (7) Å. Whatever its orientation, the geometry is awkward for the necessary hydrogen bonding, because the O(1)-N(4)-O(1) and O(3)-N(4)-O(3) angles (77.8 (5)° and 7.1 (2)°, respectively) are so small that near tetrahedral angles at the hydrogens result.

Two NH_4^+ sites in this structure appear to be relatively unfavorable. One is similar to that found in dehydrated crystals of Na_{12}-A,[5,11] Cs_9Tl_3-A,[6] and K_{12}-A,[12] deep in the large cavity opposite a 4-ring. As mentioned earlier, this position is ill-suited for an NH_4^+ ion, because it can approach only two framework oxygens and even those hydrogen bonds are far from linear. The second site is an unusual one, opposite a 6-ring that is already associated with an NH_4^+ ion. In the idealized model of this structure, these two sites are equally populated with half of an NH_4^+ ion per pseudocell. Apparently, the twelfth ammonium ion selects one of these two sites. The fact that they are approximately equally populated suggested that they have comparable energies. Such equal populations could be a feature of the ordering which causes violations of the *c* glide condition to be seen in the diffraction data.

It might be expected that at least one of the two ammonium ions sharing the oxygens of a single 6-ring would adjust its position to maximize the intercationic distance across the 6-ring plane. The elongation of the thermal ellipsoid for N(1) suggests that the sodalite-unit NH_4^+ ion does so more readily. Although it is possible that the two NH_4^+ ions hydrogen bond to the same three oxygens, it is also possible that one approaches the O(3) oxygens of the 6-ring while the other approaches the O(2) oxygens. In view of the N(1)-O(2) and N(2)-O(2) distances (3.46 and 3.22 Å, respectively), the NH_4^+ ion at N(2) appears to be best suited for such a reorientation. This arrangement was not supported by the least-squares refinement of hydrogen occupancies, which indicated that none of the threefold axis NH_4^+ ions were directed at O(2) oxygens. However, since only a half of a NH_4^+ ion per pseudocell is involved, it might be argued that the occupancy refinement was not a very sensitive probe. Alternatively, the two NH_4^+ ions could simply be twisted somewhat so their hydrogens are not eclipsed. But, once again, this hypothesis was not supported by least-squares refinement.

The N(2)-O(3) distance of 2.79 Å agrees relatively well with the sum of the ionic radii (1.43 + 1.32 = 2.75 Å).[22] However, the N(1)-O(3), N(3)-O(1), and N(4)-O(1) distances (2.99, 2.93, and 3.20 Å, respectively), while still in the range of reported NH-O distances, are somewhat longer. In many zeolite A structures, the large-cavity cations associated with 6-rings make significantly shorter approaches to framework oxygens than do their sodalite unit counterparts. This may be due to the more surface-like nature of the large-cavity position. The N(1) position (in the sodalite unit) is also likely to be a weighted average of at least two positions because of the doubly occupied 6-ring, and therefore the sodalite-unit NH_4^+ ions in the singly occupied 6-rings appear to be further from the framework than they are in reality. The 8-ring NH_4^+ ions each make two similarly long hydrogen bonds to framework oxygens; these longer approaches allow both hydrogen bonds to be nearly linear. Finally, the N(4) position is ill-suited for an NH_4^+ ion, and it might be anticipated that interactions with framework oxygens would be weakened by simple geometric considerations. There is probably a certain amount of distortion of the particular 4-ring involved, but because this affects only 0.5 of the 12 4-rings per pseudocell (ca 4%), and because only an average geometry is determined crystallographically, that distortion is not observed.

It was hoped that refinement in *Fm*3*c* would allow the NH_4^+ hydrogens to be located. This hope was realized only in part. Exact hydrogen positions could not be discerned, but the simple addition of calculated positions to the structural model did permit tentative conclusions about the orientation of the NH_4^+ ions to be drawn and did allow the otherwise obscure N(4) position to be located.

It was apparent from the outset, however, that the space group *Fm*3*c* was not correct. Of the 107 observed (at the 2σ level) *b* reflections, 30 violate the *c* glide condition for *Fm*3*c* (Table I). Similar violations have been observed in hydrated Ca_6-A[22] (65 out of 180 at the 1σ level), dehydrated Na_{12}-A[11] (5 out of 109 at the 2σ level), and dehydrated K_{12}-A[12] (4 out of 97 at the 2σ level). None were reported in hydrated Na_{12}-A.[10] In the structures of the dehydrated sodium and potassium zeolites, the inconsistencies were considered minor and were ignored, but for Ca_6-A and for the present case, their significance cannot be denied. Apparently the arrangement of these cations within the zeolite A lattice is ordered in such a way as to violate the *c* glide symmetry of the framework atoms. This means that the assumption that the cations are disordered over all *Fm*3*c* equipoints is not strictly valid.

Numerous cation distribution models were examined, but no chemically sensible arrangement consistent with only a *c* glide violation of *Fm*3*c* was found. In fact, most models reduced the symmetry all the way to *P*1. One of the simplest models consisted of sodalite units like the one shown in Figure 3 alternating in all three dimensions (via double 4-rings) with similarly oriented sodalite units having no doubly occupied 6-rings (NH_4^+ ion at N(2) missing). In those large cavities with no doubly occupied 6-ring, an NH_4^+ ion was placed at N(4). This arrangement has no two-, three-, or four fold axes, no mirror or glide planes, no screw axes, and no inversion center. It is triclinic. In the 24.568-Å cubic unit cell, this distribution would obey a face-centering condition (its true unit cell has one-fourth the volume of this one) and would violate a *c* glide condition. Although this model would account for the experimental observation of face-centering systematic absences and for the absence of *c* glide systematic ab-

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sences, it does not have the cubic symmetry that the intensity measurements indicated. It also requires a 3.0-Å contact distance between NH_4^+ ions at N(2) and N(4) in half of the large cavities. To preserve the cubic symmetry and to avoid the short intercationic approach, we must assume some disorder of the NH_4^+ ions.

It has been assumed that all exchangeable cations in this structure are NH_4^+, none H_3O^+.[8] The high pH during ion exchange and the high stability of NH_4^+ relative to H_3O^+ support this assumption, that all exchangeable cations (except for much less than 1 out of 12) in the solvated crystal where NH_4^+ and that desolvation at 25 °C removed only excess NH_3 (If present) and H_2O; that is, NH_4^+ did not hydrolyze to any significant extent to form H_3O^+ and NH_3 vapor (the *pK* for this hydrolysis would be 9.26 at 25 °C in aqueous solution). This experiment is not able to distinguish between N and O.

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Supplementary Material Available: A listing of the observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Characterization of Apical Copper(II)-Thioether Bonding. Structure and Electronic Spectra of Bis(2,2-bis(5-phenyl-2-imidazolyl)propane)copper(II) Diperchlorate and Bis(1,3-bis(5-phenyl-2-imidazolyl)-2-thiopropane)copper(II) Diperchlorate

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Abstract: The crystal and molecular structures of bis(2,2-bis(5-phenyl-2-imidazolyl)propane)copper(II) diperchlorate tetramethanolate (**1**) and bis(1,3-bis(5-phenyl-2-imidazolyl)-2-thiopropane)copper(II) diperchlorate pentamethanolate (**2**) have been determined from single-crystal, three-dimensional X-ray data collected by counter methods. Complex **1** crystallized from CH_3OH as light brown prisms in space group $P\bar{1}$ with $Z = 1$, $a = 11.064$ (5) Å, $b = 13.469$ (7) Å, $c = 9.018$ (3) Å, $\alpha = 105.85$ (4)°, $\beta = 104.85$ (4)°, $\gamma = 85.58$ (4)°, $d_{calcd} = 1.393$ g/cm^3, and $d_{obsd} = 1.43$ (5) g/cm^3. Least-squares refinement of 2411 reflections having $F_o^2 > 3\sigma(F_o^2)$ gave a conventional R factor of 0.064. The structure contains discrete Cu(II) monomers having planar N_4 ligand donor sets with Cu-N bond distances of 1.979 (5) and 1.960 (4) Å. The ClO_4^- and CH_3OH groups are lattice species well removed from the copper atoms. Complex **2** crystallized from CH_3OH as orange-brown prisms in space group $P2_1/c$ with $Z = 2$, $a = 12.08$ (2) Å, $b = 11.98$ (2) Å, $c = 18.93$ (3) Å, $\beta = 96.19$ (4)°, $d_{calcd} = 1.360$ g/cm^3, and $d_{obsd} = 1.43$ (5) g/cm^3. Least-squares refinement of 2351 reflections having $F_o^2 \geq 3\sigma(F_o^2)$ gave a conventional R factor of 0.089. The structure contains discrete Cu(II) monomers having tetragonal N_4S_2 ligand donor sets with equatorial Cu-N bond distances of 2.020 (9) and 2.019 (7) Å and apical Cu-S bond distances of 2.824 (5) Å. Electronic and ESR spectra are reported for **1** and **2**. Electronic spectra also are reported for bis(1,2-bis(5-phenyl-2-imidazolyl)ethane)copper(II) diperchlorate (**3**) and bis(1,3-bis(5-*tert*-butyl-2-imidazolyl)-2-thiopropane)copper(II) diperchlorate (**4**). In contrast to the prominant ($\epsilon > 1000$) ligand to metal charge-transfer (LMCT) absorption at ~25 000 cm^{-1} exhibited by equatorial thioether-Cu(II) units (Cu-S = ~2.3 Å), the corresponding absorptions anticipated for complexes **2** and **4** were too weak to detect. Complexes **1-4** all exhibit a weak ($\epsilon \approx 200$) absorption at ~25000 cm^{-1} attributable to poorly resolved π(imidazole) → Cu(II) LMCT. The assignments of thioether → Cu(II) LMCT proposed for plastocyanin and other type 1 copper proteins are reconsidered in view of the above spectroscopic results and the available protein crystallographic data.

The peculiar coordination structures and properties of the Cu(II) sites in the type 1 proteins now are fairly well-defined. Crystallographic studies at ~3 Å resolution of azurin[2] and plastocyanin[3] have shown that the Cu(II) in both proteins is ligated by a distorted tetrahedral arrangement of two imidazole (ImH) nitrogens (N), a cysteine sulfur (S), and a methionine sulfur (S*) atom. Further study of plastocyanin at ~1.6 Å resolution[4] has revealed that the Cu-S* bonding effectively is apical (~2.9 Å); other bond distances within the CuN_2SS^* fragment are normal. Moreover, bond angles within the CuN_2SS^* fragment generally are highly distorted from the ideal 109° value. Detailed electronic spectral studies of azurin, plastocyanin, and stellacyanin recently have been published.[5] Ligand field absorptions of the Cu(II) sites fall in the 5000-11 000 cm^{-1} spectral range. Characteristic absorptions of these proteins at ~*13* 000 and ~*16* 000 cm^{-1} convincingly have been assigned to π(S) → Cu(II) and σ(S) → Cu(II)

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