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Registry No. $H_2NOSO_3^-$, 41380-12-5; $H_2NSSO_3^-$, 49559-18-4; $CH_3NHOSO_3^-$, 41380-13-6; $S_2O_3^{2-}$, 14383-50-7; $(H_2N)_2CS$, 62-56-6; H_2NSSO_3K, 49559-20-8; $[(H_2N)_2CSNH_2]_2SO_4$, 49559-21-9.

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Five-Coordinate and Three-Coordinate Manganese(II). Hydrated and Dehydrated Crystal Structures of Partially Manganese(II)-Exchanged Zeolite A

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The crystal structures of hydrated (a = 12.268 (4) Å) and vacuum-dehydrated (a = 12.175 (3) Å) Mn(II)-exchanged zeolite A have been determined by single-crystal X-ray diffraction techniques in the cubic space group *Pm*3*m*. Chemical analyses revealed 4.5 Mn(II) ions per unit cell following an exchange period of either 3 weeks or 3 months. The 4.5 Mn(II) ions are distributed over an eightfold equipoint on threefold axes near the centers of the six-oxygen windows in each structure. In the hydrated structure, the probable positions of 29.5 water molecules have been determined and the Mn(II) ions are found to be pentacoordinate in a trigonal-bipyramidal manner: axially by two water molecules of hydration and in the plane by three framework oxygen atoms. These Mn(II)–O closest approaches are 2.03 (6) and 2.06 (7) Å to the two axial (water) ligands and 2.28 (1) Å to the three equivalent oxygen atoms. In the dehydrated material, only the latter three donor atoms remain, and Mn(II) ions coordinate to these at distances of 2.11 (1) Å in a near trigonal-planar manner. In the dehydrated structure, the remaining three Na^+ ions, also three-coordinate, are located in the otherwise unoccupied six-oxygen windows.

Introduction

By determining the structures of transition metal ion exchanged zeolite 4A, the unusual coordination geometries of these ions in an unaccommodating medium may be learned. Also the changes in the aluminosilicate framework itself under varying degrees of ion exchange and dehydration can be observed. Furthermore, complexes of the dehydrated materials can be prepared which should elucidate the structural basis for their pronounced catalytic activity in a wide range of chemical processes.

Different limits to the degree of cation exchange have been noted,[1-4] indicative either of the formation of stable ion and solvent configurations within the zeolitic channels and cavities or perhaps of a natural limit to the unevenness of positive charge distribution stabilizing the anionic framework.

A preliminary account of this work has been reported.[5]

Experimental Section

Two exchange experiments were done, one for 3 weeks and one for 3 months. In each trial approximately 0.5 g of cubic single crystals (0.03–0.07 mm on an edge), previously prepared,[1,2,6,7] were allowed to exchange at 28° with 50 ml of a 0.1 *M* solution of $Mn(ClO_4)_2 \cdot 6H_2O$). Both samples were placed in solutions containing a large excess of Mn(II) ions and were periodically agitated to ensure a uniform Mn(II) ion concentration in the vicinity of the crystals. In both cases, the crystals were pinkish tan. Subsequent chemical analyses revealed 4.4 Mn(II) ions per unit cell for the 3-week exchange and 4.5 Mn(II) ions for the 3-month exchange. Apparently the exchange, which is initially rapid, stops or slows appreciably after about 4.5 Mn(II) ions per unit cell have entered the structure. This limits the number of remaining Na^+ ions to 3 and results in the following unit cell stoichiometry, $[Mn^{2+}{}_{4.5}Na^+{}_3(Si_{12}Al_{12}O_{48})^{12-}] \cdot xH_2O$. This structure will be referred to henceforth as Mn[A].

A cubic single crystal 0.0065 cm on an edge was mounted at the tip of a glass fiber and maintained at 20° and a relative humidity of 30%. Diffraction intensities were collected using graphite-monochromatized Mo Kα radiation (Kα_1, λ 0.70926 Å; Kα_2, λ 0.71354 Å). The second crystal, 0.0070 cm on an edge, was prepared by a procedure similar to that employed before[6] in dehydrating zeolite 4A. The capillary containing the single crystal was sealed off under vacuum after a 24-hr dehydration period at 350° and 10^{-5} Torr. Upon dehydration, the color of the crystal became tan, without a pink component. Subsequent diffraction intensities were collected at 19° for $0° < 2\theta < 70°$. The space group *Pm*3*m* (no systematic absences) was used instead of $Fm\bar{3}c$ for reasons discussed earlier.[1,2,6-8]

A Syntex four-circle computer-controlled diffractometer with a pulse height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. In each case the cubic cell constants, a = 12.268 (4) Å for the hydrated crystal and a = 12.175 (3) Å for the dehydrated one, were determined by a least-squares treatment of 15 intense reflections for which $20° < 2\theta < 24°$.

The θ–2θ scan technique was employed with a scan rate (ω) variable, under computer control, between 0.5 and 24°/min in 2θ. More time was spent on the weaker reflections to minimize their standard deviations. All unique reciprocal lattice points (881 and 862 for the hydrated and dehydrated crystals, respectively) for which $2\theta < 70°$ were examined. The high upper limit was chosen for 2θ to maximize the size of the data sets even though few reflections with large 2θ values showed significant intensity. Half of the total scan time for each reflection was spent counting background at each end of the scan range, which varied from 2.0° at 2θ = 3° to 2.5° at 2θ = 70°. Two check reflections, monitored after every 100 reflections during the course of data collection, showed no significant trends in intensity.

Standard deviations were assigned according to the formula

$$\sigma(I) = [\omega^2\{\mathrm{CT} + 0.25(t_c/t_b)^2(B_1 + B_2)\} + (pI)^2]^{1/2}$$

where CT is the total integrated count obtained in a scan time of t_c, B_1 and B_2 are the background counts each obtained in time t_b, and $I = \omega[\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)]$. A value of 0.02 was assigned to the empirical parameter p to account for instrument instability. The net counts were then corrected for Lorentz and polarization effects. Absorption corrections were unnecessary: μ = 12.8 and 12.5 cm^{-1} for the hydrated and dehydrated crystals, respectively, and transmission coefficients ranged from 0.921 to 0.930 and from 0.916 to 0.926.

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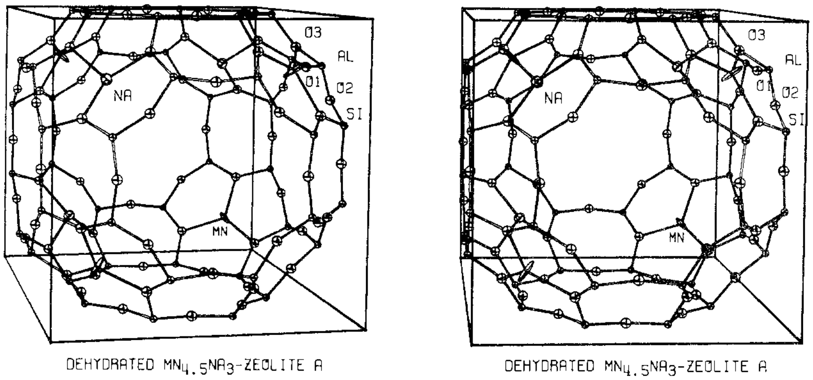

Figure 1. A stereoview of the dehydrated Mn[A] unit cell. The trigonal approaches made by Mn(II) and Na^+ to framework oxygen atoms are indicated by solid lines. Ellipsoids of 20% probability are used.

Structure Determination

Dehydrated Mn[A]. Initial full-matrix least-squares refinement of the dehydrated Mn[A] zeolite using the framework and anisotropic Mn(II) ion parameters from the hydrated Mn[A] structure, which was determined first, quickly converged at an R_1 index, $(\Sigma |F_o - |F_c||/\Sigma F_o)$, of 0.099 and a corresponding weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.115. A subsequent Fourier synthesis was particularly featureless except for four small peaks at (0, 0, 0), (0.21, 0.21, 0.21), (0, 0, 0.23), and (0.33, $^1/_2$, $^1/_2$). Only the first two positions refined at or near their observed positions with credible thermal parameters. The position at the origin, (0, 0, 0), although it refined to lowered error functions (from 0.092 to 0.087 for R_1 and from 0.110 to 0.096 for R_2, respectively), was not included in the final structure because of its low and insignificant occupancy (0.10 (5) Mn(II)), and because of its remote position with respect to all other atoms.

The inclusion of the second peak at (0.21, 0.21, 0.21), judged from its location to be assignable to the three Na^+ ions, lowered the error indices, R_1 and R_2, to the final values of 0.076 and 0.087, respectively. The anisotropic thermal parameters used were those of Na(1) in the dehydrated 4A structure,[6] since in both structures the Na^+ ions refined to the same position, and were not allowed to vary further because of their virtual proximity (0.6 Å), due to disorder, to the Mn position. Interchanging the form factors for the positions designated Na and Mn in Table I, as the thermal parameters suggest, caused rapid well-behaved divergence in least-squares. The goodness of fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 1.13; *m* is the number of observations, and *s* is the number of variables in least squares. All shifts in the final cycles of least-squares were less than 1% of their corresponding esd's. The final structural parameters are presented in Table I and a listing of the observed and calculated structure factors is available.[9] The structure is shown in Figures 1 and 2. All 163 reflections significant at the 3σ level were used throughout except for 5,12,13 which was in apparent error.

For dehydrated Mn[A], the largest peak on the final difference Fourier function, whose estimated standard deviation is 0.15 e$^-$/Å^3, was 2.3 e$^-$/Å^3 in height and was located at the origin (its refinement is discussed above). Four other peaks with heights between 0.6 and 0.8 e$^-$/Å^3 appeared also, at (0.0, 0.0, 0.23), (0.20, 0.20, 0.20), (0.33, 0.33, 0.33), and (0.33, $^1/_2$, $^1/_2$). All five of the above peaks were unusually narrow and hence apparently not indicative of new atomic positions with an approximate width at half-height of 0.3–0.4 Å.

Table I. Positional, Thermal, and Occupancy Parameters for Dehydrated Mn[A][a]

Atom	Position	*x*	*y*	*z*	*B*, Å^2, or b_{11} and b_{12}	Occupancy factor
(Si,Al)	24(k)	0	0.183 (1)	0.368 (1)	1.45 (6)	1[b]
O(1)	12(h)	0	0.198 (2)	$^1/_2$	3.0 (4)	1
O(2)	12(i)	0	0.296 (1)	0.296 (1)	2.7 (4)	1
O(3)	24(m)	0.113 (1)	0.113 (1)	0.325 (1)	3.0 (3)	1
Mn	8(g)	0.178 (1)	0.178 (1)	0.178 (1)	0.014 (1) 0.025 (2)	(4$^1/_2$)/8
Na	8(g)	0.205	0.205	0.205	0.007 0.002	3/8

[a] Standard deviations are in the units of the least significant digit given for the corresponding parameter. For Mn, the anisotropic temperature factor is $\exp[-b_{11}(h^2 + k^2 + l^2) - b_{12}(hk + hl + kl)]$. [b] The occupancy of Al is $^1/_2$, as is that of Si.

Hydrated Mn[A]. Using framework parameters from the 32 NH_3 complex[8] of zeolite 4A, initial full-matrix least-squares refinement of the hydrated Mn[A] zeolite quickly converged to R_1 and R_2 indices of 0.27 and 0.45, respectively. Successive difference Fourier syntheses and least-squares refinements served to reveal the positions of the 4.5 Mn(II) ions at (0.20, 0.20, 0.20) and 12 water molecules distributed equally between two equipoints, six at (0.10, 0.10, 0.10) and six at (0.27, 0.27, 0.27). Anisotropic least-squares refinement of Mn(II) further reduced the R_1 and R_2 indices to 0.14 and 0.13, respectively. The examination of the subsequent Fourier synthesis indicated several peaks at positions possibly appropriate for water molecules at (0, $^1/_2$, $^1/_2$), (0.23, 0.30, $^1/_2$), (0.23, $^1/_2$, $^1/_2$), ($^1/_2$, $^1/_2$, $^1/_2$), and (0, 0, 0). By the cautious least-squares refinement of the positional, thermal, and occupancy parameters of these peaks, the R_1 and R_2 indices were each further reduced to 0.10. The position ($^1/_2$, $^1/_2$, $^1/_2$) was discarded due to its negligible effect on the error indices and the poor (very long) distances it makes to other atoms. The six "water" positions found at this point were extensively and carefully examined to discern which of them might be the Na^+ site and whether the placement of molecules off *n*-fold axes (*n* = 2, 3, or 4) could better describe the structure. The error indices indicated that the additional parameters were unjustified, except for (0, $^1/_2$, $^1/_2$), which refined to (0.06, 0.43, $^1/_2$), thereby lowering the error indices and demonstrating more reasonable interatomic distances. The final values of the R_1 and R_2 indices are 0.10 and 0.095. The goodness of fit is 1.46. All 205 reflections which were significant at the 3σ level were used throughout, except for 2,6,15 which was in apparent error. The final structural parameters are presented in Table II and a listing of the observed and calculated structure factors is available.[9] The structure is partially shown in Figures 2 and 3 and is given fully in Figure 4.

The largest peak on the final difference Fourier function for hydrated Mn[A] was 1.1 e$^-$/Å^3 in height and was located at ($^1/_2$, $^1/_2$, $^1/_2$). Three other peaks of height 0.5 e$^-$/Å^3, approximately 3 times the esd (0.15 e$^-$/Å^3) of this Fourier function, were also present.

The full-matrix least-squares program[10] used in both structure determinations minimizes $\Sigma w(\Delta |F|)^2$; the weights (*w*) were the reciprocal squares of σ, the standard deviation of each observation. Atomic scattering factors[11] for Mn^+, Na^+, Si^{2+}, $Al^{1.5+}$, and O^- were used. The values for Mn^+ were increased by 0.3–0.4 electron to account for the real component of anomalous dispersion. The X(1), X(2), and X(3) positions (see the Discussion) were refined using O^- scattering factor tables.

Discussion

In the dehydrated structure (see Table III and Figures 1 and 2), the cations, 4.5 Mn(II) and 3 Na^+ ions, are located on threefold axes close to the planes of the six-oxygen windows. (A general discussion of the structure of zeolite A and of the terms used in its description is available.[6]) The Mn(II) ions are recessed 0.108 Å into the sodalite unit from the [111]

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(9) See paragraph at end of paper regarding supplementary material.

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Table II. Positional, Thermal, and Occupancy Parameters for Hydrated Mn[A][a]

Atom	Position	x	y	z	B, A^2 or b_{11} and b_{12}	Occupancy factor
(Si,Al)	24(k)	0	0.183 (1)	0.371 (1)	1.0 (1)	1^b
O(1)	12(h)	0	0.221 (2)	$^1/_2$	2.7 (4)	1
O(2)	12(i)	0	0.293 (1)	0.293 (1)	2.1 (3)	1
O(3)	24(m)	0.113 (1)	0.113 (1)	0.339 (1)	3.2 (3)	1
Mn	8(g)	0.199 (1)	0.199 (1)	0.199 (1)	0.008 (1) 0.002 (1)	$(4^1/_2)/8$
$H_2O(1)$	8(g)	0.104 (3)	0.104 (3)	0.104 (3)	4.5 (11)	$(4^1/_2)/8$ (0.07)[c]
$H_2O(2)$	8(g)	0.297 (3)	0.297 (3)	0.297 (3)	7.3 (15)	3/4 (0.08)[c]
$H_2O(3)$	24(l)	0.219 (7)	0.317 (8)	$^1/_2$	14.5 (26)	1/2 (0.07)[c]
X(1)[d]	24(l)	0.060 (11)	0.429 (10)	$^1/_2$	3.7 (23)	1/8 (0.04)[c]
X(2)[d]	6(f)	0.239 (5)	$^1/_2$	$^1/_2$	2.8 (11)	1/2 (0.07)[c]
X(3)[d]	1(a)	0	0	0	6.4 (28)	1 (0.26)[c]

[a] Standard deviations are in the units of the least significant digit given for the corresponding parameter. For Mn, the anisotropic temperature factor is $\exp[-b_{11}(h^2 + k^2 + l^2) - b_{12}(hk + hl + kl)]$. [b] The occupancy of Al is $^1/_2$, as is that of Si. [c] These occupancy parameters were selected based on packing, coordination, and hydrogen bonding considerations and upon the physical reasonability of the thermal parameters which correlate well with them and which could not be refined independently in this case. The occupancy parameters were allowed to vary for one least-squares cycle so that their standard deviations could be calculated. The shifts to irrational numbers were less than these esd's and were not used. [d] The atomic scattering factors used were those of O^-.

Table III. Interatomic Distances and Angles[a] for Dehydrated Mn[A]

(Si,Al)-O(1)	1.62 (1)[b]	Mn-O(2)	2.97 (1)
(Si,Al)-O(2)	1.64 (1)	Na-O(3)	2.16 (5)
(Si,Al)-O(3)	1.70 (1)	Na-O(2)	2.95 (2)
Mn-O(3)	2.11 (1)		
O(1)-(Si,Al)-O(2)	115.5 (8)[c]	(Si,Al)-O(2)-(Si,Al)	154.7 (14)
O(1)-(Si,Al)-O(3)	111.5 (9)	(Si,Al)-O(3)-(Si,Al)	135.7 (9)
O(2)-(Si,Al)-O(3)	105.0 (7)	O(3)-Mn-O(3)	119.6 (1)
O(3)-(Si,Al)-O(3)	107.8 (10)	O(3)-Na-O(3)	115.5 (7)
(Si,Al)-O(1)-(Si,Al)	166.3 (7)		

[a] Standard deviations are in the units of the least significant digit given for the corresponding parameter. [b] Interatomic distances are in angstroms. [c] Angles are in degrees.

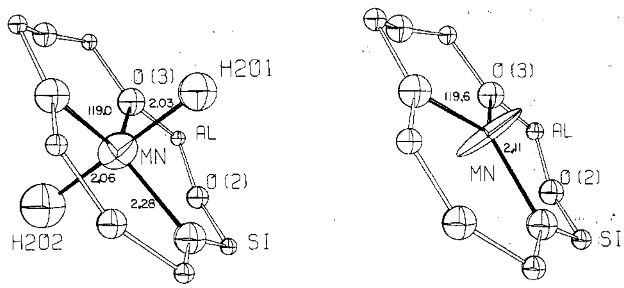

Figure 2. Equivalent Mn(II)-occupied six-oxygen windows of dehydrated Mn[A] (right) and of the hydrated Mn[A] structure (left). The coordination about Mn(II) is indicated by solid lines. Ellipsoids of 20% probability are used.

plane at O(3). The Na^+ ions are 0.46 Å from the same plane but are recessed into the large cavity, perhaps because of repulsive forces from the heavier cations partially in the sodalite unit. Both Mn(II) and Na^+ ions are trigonally coordinated to respective sets of three framework O(3)'s at 2.11 (1) and 2.16 (5) Å, respectively; the Mn(II) ions demonstrate nearly trigonal-planar coordination.

It is plausible to believe that the conformation of a particular six-oxygen window depends on whether Mn(II), Na^+, or no cation is situated near its center. In this work, only the weighted-average conformation has been determined. While this may be close to that of the Mn(II)-associated six-oxygen window, it should be further from that of a Na^+-associated window. For this reason, the O(3)-Na^+ distance, in particular, may be inaccurate, perhaps too short.

In hydrated Mn[A] (see Table IV), 29.5 water molecules distributed among six equipoints were located and refined. In the sodalite unit, 4.5 water molecules are at $H_2O(1)$, Wyckoff position 8(g), coordinating the Mn(II) ions in the six-oxygen windows and simultaneously forming hydrogen bonds (each water molecule can form two, each 2.89 (4) Å in length) to the framework O(3)'s. Similar cation coordination and hydrogen-bonding opportunities are available to the six water molecules at $H_2O(2)$, Wyckoff position 8(g), located on the threefold axes in the large cavity. The two Mn(II)-OH_2 distances are equal: 2.03 (6) and 2.06 (7) Å for $H_2O(1)$ and $H_2O(2)$. The three symmetry-equivalent Mn(II) to framework O(3) distances are 2.28 (1) Å, affording the Mn(II) ions a nearly regular trigonal-bipyramidal coordination sphere[12-15] (see Figures 2 and 3). The Mn(II) ions are 0.24 Å from the [111] plane at O(3), in sharp contrast to the deviations observed for the cations Na^+, Ni(II), Co(II), and Zn(II): 0.52,[16] 1.53,[4] 1.65,[2] and 0.54[3] Å, respectively. These results indicate that Mn(II) ions do not find nearly trigonal-bipyramidal coordination unfavorable. The water molecules at $H_2O(2)$ may also hydrogen bond to 12 water molecules at $H_2O(3)$, Wyckoff positions 24(l), at a distance of 2.68 (4) Å, forming an irregular and incomplete version of the pentagonal dodecahedra reported earlier.[16,17]

The stereoviews of Figures 1, 3, and 4 were prepared using ORTEP.[18]

The 3 Na^+ ions could not be definitively assigned to one of the equipoints X(1), X(2), or X(3), which would otherwise contain water oxygen atoms. The equipoint X(1), Wyckoff 24(l), is the least favorable because of a long approach distance of 2.66 (13) Å to O(1) and is more appropriate for a water oxygen. The equipoint X(2), Wyckoff 6(f), is the most likely site for Na^+. It lies on a fourfold axis 2.26 (9) Å from $H_2O(3)$ at a site which may bridge[16,17] two $H_2O(3)$'s involved in the dodecahedron (see Figure 4). X(2) can simultaneously coordinate X(1) at a distance of 2.36 (15) Å. The position X(3), at the origin, is also unfavorable. It makes a distance of 2.21 (7) Å to 4.5 $H_2O(1)$'s, which are already involved in Mn(II) coordination.

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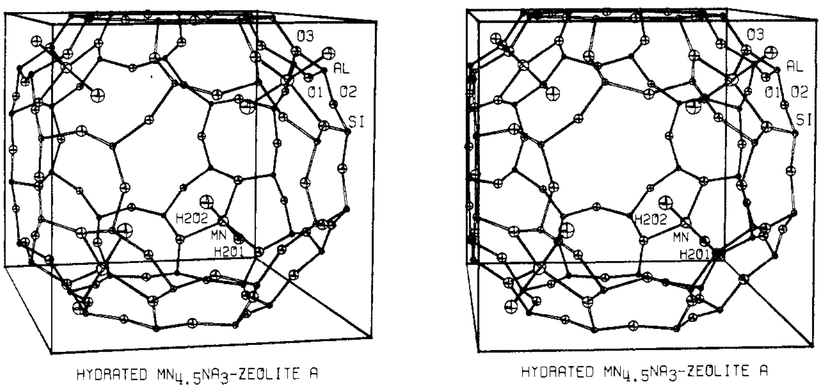

Figure 3. A stereoview of the hydrated Mn[A] unit cell is shown. The trigonal-bipyramidal coordination about Mn(II) is indicated by solid lines. For clarity, only the water molecules which participate in coordination are included. Ellipsoids of 20% probability are used.

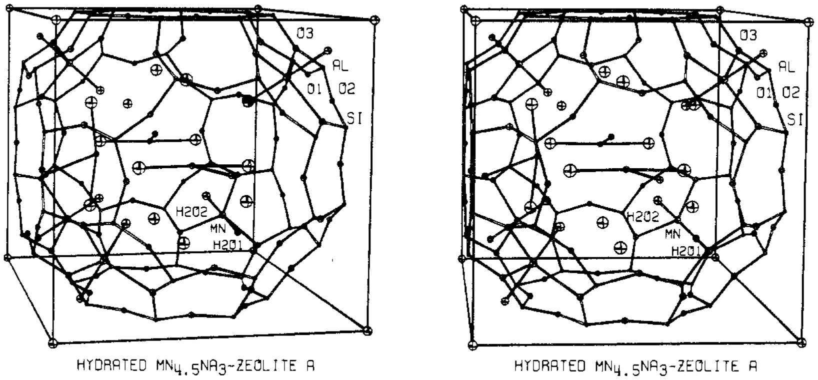

Figure 4. Stereoview of hydrated Mn[A] including all cations and water molecules. Ellipsoids of 5% probability are used.

Table IV. Interatomic Distances and Angles[a] for Hydrated Mn[A]

(Si,Al)-O(1)	1.65 (1)[b]	$H_2O(2)$-O(3)	3.23 (5)
(Si,Al)-O(2)	1.65 (1)	$H_2O(2)$-$H_2O(3)$	2.68 (4)
(Si,Al)-O(3)	1.68 (1)	$H_2O(3)$-X(2)	2.26 (9)
Mn-O(3)	2.28 (1)	$H_2O(3)$-X(1)	2.39 (16)
Mn-$H_2O(1)$	2.03 (6)	$H_2O(3)$-O(1)	2.93 (9)
Mn-$H_2O(2)$	2.06 (7)	$H_2O(3)$-O(2)	3.70 (6)
$H_2O(1)$-O(3)	2.89 (4)	X(1)-O(1)	2.66 (13)
$H_2O(1)$-X(3)	2.21 (7)	X(1)-X(2)	2.36 (15)
O(1)-(Si,Al)-O(2)	109.0 (7)[c]	X(1)-X(2)-$H_2O(3)$	105.1 (30)
O(1)-(Si,Al)-O(3)	111.4 (5)	O(1)-X(1)-O(1)	100.1 (39)
O(2)-(Si,Al)-O(3)	106.6 (8)	Mn-$H_2O(2)$-$H_2O(3)$	112.6 (33)
O(3)-(Si,Al)-O(3)	111.4 (10)	$H_2O(3)$-$H_2O(2)$-$H_2O(3)$	130.8 (37)
(Si,Al)-O(1)-(Si,Al)	147.5 (6)	O(1)-$H_2O(3)$-O(2)	106.8 (29)
(Si,Al)-O(2)-(Si,Al)	160.6 (12)	O(1)-$H_2O(3)$-X(2)	120.0 (22)
(Si,Al)-O(3)-(Si,Al)	142.8 (10)	O(1)-$H_2O(3)$-$H_2O(3)$	106.5 (18)
O(3)-Mn-O(3)	119.0 (1)	$H_2O(1)$-X(3)-$H_2O(1)$	109.5 (28)
O(3)-$H_2O(2)$-O(3)	74.9 (9)	O(3)-Mn-$H_2O(1)$	84.1 (7)
$H_2O(1)$-Mn-$H_2O(2)$	180.0 (26)	O(3)-Mn-$H_2O(2)$	95.9 (19)

[a] Standard deviations are in the units of the least significant digit given for the corresponding parameter. [b] Interatomic distances are in angstroms. [c] Angles are in degrees.

Another more detailed interpretation of these results is possible. Perhaps there are two types of "unit cells," one containing 5 Mn(II) ions and the other with 4. The 4 Mn(II) ion cell might have a Na^+ ion at the origin and up to 8 water molecules at or near $H_2O(1)$. This arrangement would allow the Na^+ ion to be tetrahedrally associated with up to 4 water molecules. The remaining 3 Na^+ ions would be at X(2). In the nonequivalent 5 Mn(II) ion "unit cell," no cation would be at the origin and 5 water molecules would be at or near the $H_2O(1)$ position. The 2 Na^+ ions would be at X(2).

Table V. Deviation of Atoms from the 111 Plane of O(3) of Hydrated and Dehydrated Mn[A] (in Å)[a]

	Dehydrated	Hydrated
Mn	−0.11	0.24
Na	0.46	
O(2)	0.29	0.15
$H_2O(1)$		−1.79
$H_2O(2)$		2.30

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

Table VI. Angles (Si,Al)-O-(Si,Al) at Oxygen[a]

	O(1)	O(2)	O(3)
Na[A], hydrated[b]	146	160	144
Mn[A], hydrated	148	161	143
Na[A], dehydrated[c]	145	166	146
Mn[A], dehydrated	166	154	135

[a] Standard deviations are 1° or less. [b] Reference 16. [c] Reference 6.

General Comparisons

The major difference between the hydrated and dehydrated structures is the location of Na^+ ions. The positions of the Mn(II) ions are not appreciably affected by hydration, but the Na^+ ions move far from their six-oxygen window threefold axis positions into the large cavity, probably to the X(2) positions to perform a bridging function as reported earlier.[16,17]

Lesser changes upon dehydration include the movement (by 0.35 Å; see Table V) of Mn(II) ions to positions recessed slightly into the sodalite unit, in accord with previous findings[2] involving Co(II). Furthermore, the (Si,Al)-O bond lengths decreased for those framework oxygens O(1) and O(2) (by 1.65 (1)-1.62 (1) and 1.65 (1)-1.64 (1) Å, respectively) which are no longer associated with water or cations. A corresponding small increase is noted for O(3) (1.68 (1)- to 1.70 (1) Å) which is so involved (see Tables III and IV). There is a simultaneous decrease of the Mn(II)-O(3) internuclear distance upon dehydration, corresponding to the movement of the Mn(II) ions to a position closer to the plane of its nearest O(3) neighbors and to conformational changes in the six-oxygen windows.

In general, the (Si,Al)-O-(Si, Al) framework bond angles of hydrated Mn[A] (see Table VI) are very similar to those in Na[A],[16] which can be considered the least strained[1] framework orientiation. Upon dehydration, however, large changes (see Table VI) are observed which can be compared with those found in Tl(I)[1]- and Co(II)[2]- exchanged samples of zeolite A.

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Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-723.

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Linkage Isomerism of a Bridging Cyanide. Crystal Structure of Pentacyanocobalt(III)-μ-isocyano-pentaamminecobalt(III) Monohydrate

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The crystal structure of $(NH_3)_5CoCNCo(CN)_5 \cdot H_2O$ has been investigated by single-crystal X-ray techniques. Of the several crystalline modifications prepared, a form was chosen for study which is isostructural with its linkage isomer $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$. The space group is *Pbca* with $Z = 8$ and lattice constants are $a = 17.399$ (4), $b = 12.187$ (2), and $c = 13.931$ (1) Å. The calculated density is 1.696 g cm^{-3}, and the measured density is 1.68 (2) g cm^{-3}. Intensity data for 1822 reflections were measured with a Datex automated GE diffractometer using Co Kα radiation. The structure was refined by full-matrix least-squares methods to a final R index of 0.085. This study confirms that, as in the linkage isomer, there is no scrambling of unlike ligands around the two cobalt centers; in this isomer the bridging cyanide group is carbon bonded to the pentaamminecobalt species and nitrogen bonded to the pentacyanocobalt species. In general this compound exhibits longer Co-ligand distances and significantly shorter C-N distances than does its linkage isomer. The molecule is somewhat more symmetrically bent than is its linkage isomer, and a 0.03-Å shortening of the Co-C bond trans to the bridging cyanide group is noted relative to the equatorial Co-C distances. There is also some indication of a lengthening of Co-ligand distances cis to the bridging group at both cobalt atoms of this structure relative to those found in the structure of the linkage isomer.

Introduction

The crystal structure of $(NH_3)_5CoNCCo(CN)_5 \cdot H_2O$ (hereafter referred to as the cyano isomer) has been reported;[1] the molecule has a distinctly nonlinear cyano bridge and exhibits a significant shortening of the Co-N distance trans to the bridging group. Recently de Castello, Mac-Coll, and Haim have reported the synthesis of the isocyano linkage isomer by the reaction in solution[2]

$$[(NH_3)_5CoCN]^{2+} + [(CN)_5CoOH_2]^{2-} \rightarrow (NH_3)_5CoCNCo(CN)_5 + H_2O$$

The structure of this new compound was of particular interest to us due to the unique geometry of the cyano isomer. A comparison of the structure of both isomers would exhibit the effects of linkage isomerism of the cyanide ligand on bonding in both the pentaamminecobalt(III) system and the pentacyanocobalt(III) system. In order to make this comparison, to confirm that ammine and cyanide ligands are not scrambled among the two cobalt centers, and to confirm the orientation of the bridging cyanide group, a structural study of the isocyano isomer was undertaken.

Experimental Section

A sample of the compound was provided by Haim in the form of a finely divided yellow powder. Recrystallization of this powder from an ethanol-water mixture yielded tetragonal crystals of space group $P4_2$ having two molecules per unit cell with dimensions $a = 8.08$ and $c = 14.66$ Å. These crystals lost solvent and disintegrated readily upon removal from the mother liquor. Intensity data were collected for this modification with a diffractometer, but the crystal underwent anisotropic decay in the X-ray beam, and the data obtained were not of suitable quality to allow even the general features of the structure to be determined.[3]

Prismatic crystals were obtained from an aqueous acetic acid solution and were found to be orthorhombic with approximate cell dimensions $a = 11.4$, $b = 10.7$, and $c = 14.5$ Å. Systematic extinctions do not uniquely determine the space group of this form, but density and point symmetry considerations limit the possibilities to $Cmc2_1$ or $C2cm$. These crystals also lost solvent readily and disintegrated upon removal from the mother liquor.

Small, stable crystals of space group *Pbca* were obtained by recrystallization by slow evaporation from a concentrated $NaHCO_3$ solution. Oscillation and Weissenberg photographs indicated that

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