(10) M. C. Rakowski and E. L. Muetterties, *J. Am. Chem. Soc.*, **99**, 739 (1977).
(11) S. Attali and R. Poilblanc, *Inorg. Chim. Acta*, **6**, 475 (1972).
(12) (a) J. W. Rathke and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 3272 (1975); (b) T. V. Harris, J. W. Rathke, and E. L. Muetterties, *ibid.*, in press.
(13) (a) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 4545 (1972). (b) Anal. Calcd for $CoC_{12}H_{37}O_{12}P_5F_6$: Co, 8.17; C, 19.96; H, 5.17; P, 21.49; F, 15.81. Found: Co, 8.17; C, 20.68; H, 5.48; P, 22.20; F, 14.43.
(14) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); H. P. Fritz and K. E. Schwarzhaus, *J. Organomet. Chem.*, **1**, 208 (1964).
(15) H. F. Klein and H. H. Karsch, *Chem. Ber.*, **108**, 944 (1975).
(16) H. F. Klein, H. H. Karsch, and W. Buchner, *Chem. Ber.*, **107**, 537 (1974).
(17) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).
(18) J. P. Jesson and P. Meakin, *J. Am. Chem. Soc.*, **96**, 5760 (1974).
(19) C. Perdone and A. Singer, *Inorg. Chem.*, **7**, 2614 (1968); A. R. Luxmore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).
(20) S. D. Ittel, F. A. Van-Catledge, C. A. Tolman, and J. P. Jesson, *J. Am. Chem. Soc.*, **100**, 1317 (1978).
(21) C. P. Casey and C. R. Cyr, *J. Am. Chem. Soc.*, **95**, 2248 (1973).
(22) W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968).

The Octahedral Hexasilver Molecule. Seven Crystal Structures of Variously Vacuum-Dehydrated Fully Ag^+-Exchanged Zeolite A

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Abstract: The structures of seven differently vacuum-dehydrated fully Ag^+-exchanged zeolite A crystals have been determined by single-crystal X-ray diffraction techniques. Their structures were solved and refined in the cubic space group *Pm3m* at 24 (1) °C. All crystals were ion exchanged in flowing streams of aqueous $AgNO_3$, followed by dehydration at constant temperatures ranging from 395 to 475 °C for from 2 to 10 days. In two of these structures with an approximate unit-cell composition of $Ag^+_8Ag^0_4H^+_{2x}Si_{12}Al_{12}O_{46+x}$, $x \simeq 1$, eight equivalent Ag^+ ions lie at sites of near trigonal planar coordination on threefold axes very near the centers of the 6-oxygen rings. Two-thirds of the sodalite units contain octahedral Ag_6 molecules at their centers, while the remaining one-third of the sodalite units are empty of silver species. (Alternatively, contrary to the tendency of metal atoms to form clusters, and with molecular symmetry less than the site symmetry, molecules of Ag_5 or Ag_4 with an octahedral structure in which one or any two vertices are missing may exist.) The probable six-atom cluster, which is stabilized by coordination to eight Ag^+ ions, is closest packed and is a unit of the structure of silver metal. It is the smallest possible fully developed single crystal of silver, whose natural form is {111}. The Ag–Ag distance in the cluster, ca. 2.92 Å, is near the 2.89 Å bond length in silver metal. Two oxide ions per unit cell, approximately one from a position which links the sodalite units together and the other from an H_2O molecule, have been lost as O_2 as a result of decomposition to preserve charge balance. By comparison with partially hydrated fully Ag^+-exchanged zeolite A, it is observed that the populations of Ag^+ ions at 4-ring and 8-ring sites are the first to be depleted as some Ag^+ ions are reduced to Ag^0. It is also observed that the hexasilver molecule is stable within the zeolite only when it is stabilized by coordination to at least six Ag^+ ions at 25 °C or eight at ca. 450 °C.

Introduction

The structures of small clusters of some metals, notably platinum, palladium, and nickel, are of interest because of their pronounced catalytic activity. These three metals, and several others including gold, rhodium, iridium, and aluminum, are isostructural with silver.

Catalysts containing both Ag^0 and Ag^+ are important in partial oxidation processes such as the formation of ethylene oxide from ethylene and oxygen.[1] A vacuum-dehydrated sample of zeolite A, containing H^+ ions and Ag_6 clusters complexed to eight Ag^+ ions, after exposure to oxygen, partially oxidized NH_3 to form the saturated hydronitrogens N_3H_5 (triazane) and N_3H_3 (cyclotriazane).[2] These processes are indicative of a unique chemistry which is inadequately understood at present.

Metal ions in zeolites can be readily reduced. For example, Ni^{2+} ions in zeolite Y can be reduced to Ni^+ by sodium vapor, and to the metallic state by hydrogen.[3] Cu^{2+} ions in CuNa–Y were reduced to Cu^+ after treatment with carbon monoxide at elevated temperatures, while reduction of these ions by hydrogen gas gave Cu^0.[4] The dipositive cations of the relatively volatile elements Hg, Cd, and Zn can be removed as atoms from zeolite X by heating in hydrogen.[5]

Silver ions can also be reduced intrazeolitically. Tsutsumi and Takahashi[6] reported that Ag^+ ions in zeolite Y could be reduced to bulk clusters of Ag^0 after treatment with alcohols and alkylbenzene. Ag^+ ions in Ag–X and Ag–Y were also reduced after treatment with carbon monoxide at 350 °C.[7] Matsumoto et al.[8] found that Ag^+-exchanged zeolite A is thermally unstable and loses its crystal structure at a lower temperature than Na_{12}-A does.[9] According to them, the more Ag^+ ions exchanged to zeolite A, the less its thermal stability. Beyer[10] also found that about 70% of the Ag^+ ions in zeolite A were reducible by hydrogen after dehydration at 150 °C, and that about 92% of the Ag^+ ions were reducible at 330 °C. Beyer, Jacobs, and Uytterhoeven[11] reported that polynuclear cations of mean or approximate composition Ag_3^+ form upon partial reduction of dehydrated fully Ag^+-exchanged zeolite Y.

The crystal structures of vacuum-hydrated fully Ag^+-exchanged zeolite A samples were determined in order to learn the structure of fully dehydrated Ag_{12}-A for comparison with that of partially hydrated Ag_{12}-A,[9,12] whose three residual water molecules bridge between three Ag^+ ions inside the sodalite unit.[13] It was hoped that complete dehydration could be achieved and that a near zero coordinate[14-17] or zero coordinate[18-21] Ag^+ ion would be found. Decomposition of the zeolite framework or of water molecules, and the concomitant production of silver atoms, was not anticipated when this work was initiated.

The structures reported herein are those of seven differently

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Table I. A Summary of Experimental Results

crystal number	dehydrating temp °C	dehydrating period days	ultimate pressure Torr	crystal color[b]	unit cell constant, Å[c]	number of observed reflections[d]	number[e] of neutral Ag atoms per cell	number[e] of Ag^+ ions at 4-ring sites	6-ring sites	8-ring sites	R_1[e]	R_2[e]	goodness of fit[e]
1	400	4[a]	1×10^{-5}	silver[f]	12.279 (3)	225	1.91		5.16	0.39	0.111	0.091	2.30
2	395	4	2×10^{-5}	yellow	12.333 (2)	426	1.56	0.29	8.0	2.04	0.077	0.066	3.46
3	400	4	1×10^{-5}	yellow	12.296 (1)	416	2.1 (2.0)		7.4 (8.0)	1.5 (2.0)	0.106 (0.113)	0.101 (0.110)	5.29 (5.76)
4	425	10	1×10^{-5}	yellow	12.295 (1)	441	3.59 (3.5)		7.98 (8.0)	0.87 (0.5)	0.082 (0.083)	0.072 (0.076)	3.75 (3.94)
5	450	7	5×10^{-5}	yellow	12.248 (1)	286	3.5 (4.0)		7.75 (8.0)		0.082 (0.094)	0.081 (0.088)	3.03 (33)
6	475	1.6	2×10^{-5}	silver	12.148 (2)	187	2.4		6.82		0.163	0.11	5.20
7	475	7	1×10^{-5}	silver	11.42 (2)	8	2.0		2.2				

[a] Dehydrated in flowing O_2 for 2 days at 400 °C, followed by evacuation at 400 °C for 2 days. The effect of the oxygen treatment is unclear. [b] The yellow crystals were clear, and the silvered crystals were opaque. [c] The number in parentheses is the esd in the units of the least significant digit given. [d] Only those reflections for which $I > 3\sigma(I)$ were considered observed. [e] The numbers in parentheses were obtained from refinements in which the occupancies were fixed at internally consistent or stoichiometric values. [f] Crystal 1 became prematurely silver in appearance, perhaps because of the presence of small amounts of a reducing agent remaining from a previous experiment (see the text).

prepared crystals. Three of the seven sets of diffraction data are particularly large and reliable.

Experimental Section

Crystals of zeolite 4A, Na_{12}-A,[9] were prepared by Charnell's method,[22] modified by the inclusion of seed crystals from a previous synthesis. Complete Ag^+ exchange of seven zeolite A single crystals 0.080–0.085 mm on an edge was achieved by allowing 0.05 M aqueous $AgNO_3$ to flow past each crystal at the rate of approximately 1 cm/s for 4–5 days. The dehydration temperatures and periods (see Table I) differed for the seven crystals. (As the Discussion section explains, more than dehydration, some decomposition as well, occurred during this treatment.) For those crystals which were observed daily, it was noted that the clear, colorless, hydrated Ag^+-exchanged crystal initially became black. This color lightened to brick red and ultimately to clear yellow after 2–4 days. Further dehydration at higher temperatures, or for a particularly long period (17 days at 425 °C; this crystal is not one of the seven reported) caused the crystals to silver. The resulting clear and yellow, or opaque and silver-colored, crystals were sealed off the vacuum system and in their capillaries with a torch. Subsequent diffraction intensities for all crystals were collected at 24 (1) °C. Chemical analysis was not attempted because ion exchange had already been shown to be facile and complete,[23-25] even by less exhaustive procedures.

The cubic space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[26,27] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, λ = 0.709 30 Å; $K\alpha_2$, λ = 0.713 59 Å). The cubic unit cell constants of the first six crystals, as determined by a least-squares refinement of 15 intense reflections for which $19° < 2\theta < 24°$, are shown in Table I.

Because crystal 7 had a very sparse diffraction pattern, its unit-cell constant was determined by least-squares refinement of the six intense (100) reflections, for which $2\theta = 3.56°$. Its unit cell constant (11.42 (2) Å) is extremely small. This value has been corrected (decreased) by a small amount (0.01 Å) because only these very low angle reflections, which were broad and on uneven background, were used. (This correction was calculated by comparing the refined cell constants of the other six crystals with those calculated using only their (0,0,1) reflections.)

For each of the first six crystals, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$; and hlk, $h \leq l \leq k$) were examined using the θ–2θ scan technique. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} over a symmetric range from 0.8° (in 2θ) below the calculated $K\alpha_1$ peak to 0.8° above the $K\alpha_2$ maximum. (For crystal 7, the last three values were 0.5 deg min^{-1}, 1.2° (in 2θ), and 1.2°, respectively.) The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations (ca. 1%) of these check reflections were noted during the course of data collection. All unique reciprocal lattice points for which $2\theta < 70°$ were examined. (For crystal 7, all significant intensities could be observed with the criterion, $2\theta < 15°$.) The higher upper limit for 2θ was chosen to allow the data set to be more complete, even though few reflections at the largest 2θ values showed significant intensity.

The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization assuming the monochromator crystal to be half mosaic and half perfect in character; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.[28] The mean intensity for a reflection was calculated as $I = (I_{hkl} + I_{hlk})/2$, where $I_{hkl} = [CT - 0.5(t_c/t_b)(B_1 + B_2)]\ (\omega)$, CT is the total integrated count obtained in a scan time t_c, B_1 and B_2 are the background counts each measured in time t_b, and ω is the scan rate. The standard deviation of each unmerged reflection is $\sigma(I_{hkl}) = [(CT + B_1 + B_2)\omega^2 + (pI_{hkl})^2]^{1/2}$, where $p = 0.02$,[29] a value found to be appropriate for the instrumentation used. An absorption correction was judged to be negligible (μ ca. 3.5 mm^{-1}) and was not applied.[25] Other details of the data collection and reduction are the same as previously described.[25] Only the observed reflections, those whose net counts exceeded three times their corresponding esd's, were used in structure solution and refinement.

Structure Determination

Crystal 1. Full-matrix least-squares refinement was initiated using the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] and of the Ag^+ ions in partially hydrated Ag_{12}-A.[12] Anisotropic refinement of the framework atoms and Ag(1) (see Table IIa) converged to an R_1 index, $(\Sigma||F_o - |F_c||)/\Sigma F_o)$, of 0.319 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.253. The occupancies of the ions at Ag(2) and Ag(3) in partially hydrated Ag_{12}-A, which are on the threefold axes (x, x, x) at $x = 0.16$ and $x = 0.12$, refined to zero in this structure. A difference Fourier synthesis revealed a large and distinct peak at (0.0, 0.0, 0.172) with a height of 13.6 e $Å^{-3}$, esd = 0.5 e $Å^{-3}$. Anisotropic refinement including this position, Ag(2), converged to $R_1 = 0.167$ and $R_2 = 0.134$, as its occupancy converged at approximately two silver atoms or ions per unit cell with small anisotropic thermal parameters. A subsequent difference synthesis revealed three small peaks at (0.125, 0.125, 0.125), (0.0, 0.447, 0.447), and (0.419, 0.419, 0.428). The first and last were unstable in least-squares refinement, but the second refined as one-half Ag^+ per unit cell, at Ag(3). The final R values are given in Table I. The goodness of fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is also shown in Table I; m is the number of observations, and s is the number of variables in least squares. All shifts in the final cycle of least squares were less than 0.5% of their corresponding esd's. See Tables I, IIa, III, and IV for additional information.

Crystal 3. Least-squares refinement began using the silver and framework positions found in the structure of crystal 1. Full-matrix least-squares refinement with anisotropic thermal parameters quickly converged to $R_1 = 0.106$ and $R_2 = 0.101$. Subsequently, the occupancies of Ag(1), Ag(2), and Ag(3) refined to 7.36 (9), 2.11 (5), and 1.54 (9) silver atoms or ions. Because the crystal was yellow and not silvered, no silver metal had left the zeolite; therefore 12 silver atoms or ions must have remained. Accordingly these occupancies were round upward or to the nearest integer so that all 12 silver species would be placed. At this point, R_1 and R_2 converged to 0.112 and

Table II. Positional, Thermal,[a] and Occupancy Parameters

a. Crystal 1

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor
(Si,Al)	24(k)	0	1829 (7)	3700 (5)	30 (4)	28 (5)	20 (3)	0	0	−1 (7)	1[c]
O(1)	12(h)	0	2053 (27)	1/2	118 (35)	70 (26)	0 (10)	0	0	0	1
O(2)	12(i)	0	2976 (14)	2976 (14)	85 (25)	21 (9)	21 (9)	0	0	4 (24)	1
O(3)	24(m)	1109 (11)	1109 (11)	3343 (15)	50 (9)	50 (9)	63 (15)	22 (22)	40 (33)	40 (33)	1
Ag(1)	8(g)	1920 (8)	1920 (8)	1920 (8)	149 (10)	149 (10)	149 (10)	235 (18)	235 (18)	235 (18)	0.65 (3)
Ag(2)	6(e)	0	0	1658 (8)	17 (4)	17 (4)	−1 (6)	0	0	0	0.32 (2)
Ag(3)	12(i)	0	4503 (71)	4503 (71)	84 (86)	43 (52)	43 (52)	0	0	149 (10)	0.03 (1)

b. Crystal 2

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor
(Si,Al)	24(k)	0	1827 (3)	3704 (2)	17 (2)	10 (2)	12 (2)	0	0	2 (3)	1[c]
O(1)	12(h)	0	2148 (11)	1/2	54 (11)	45 (10)	18 (9)	0	0	0	1
O(2)	12(i)	0	2951 (6)	2951 (6)	26 (5)	22 (5)	22 (5)	0	0	25 (13)	1
O(3)	24(m)	1107 (5)	1107 (5)	3397 (6)	29 (4)	29 (4)	30 (6)	13 (10)	15 (7)	15 (7)	1
Ag(1)	8(g)	1915 (4)	1915 (4)	1915 (4)	80 (1)	80 (1)	80 (1)	116 (8)	116 (8)	116 (8)	1
Ag(2)	6(e)	0	0	1736 (7)	34 (4)	34 (4)	25 (9)	0	0	0	0.26 (1)
Ag(3)	12(i)	0	4348 (41)	4348 (41)	165 (91)	33 (55)	33 (55)	0	0	4 (81)	0.05 (1)
Ag(4)	12(h)	0	3979 (26)	1/2	637 (184)	27 (24)	326 (161)	0	0	0	0.12 (1)
Ag(5)	12(j)	2321 (39)	2321 (39)	1/2	142 (78)	142 (78)	0 (34)	−215 (166)	0	0	0.024 (5)

c. Crystal 3

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor fixed[d]	occupancy factor varied
(Si,Al)	24(k)	0	1839 (4)	3695 (4)	29 (4)	18 (4)	28 (4)	0	0	13 (6)	1[c]	1[c]
O(1)	12(h)	0	2119 (17)	1/2	108 (23)	61 (19)	3 (11)	0	0	0	1	1
O(2)	12(i)	0	2943 (11)	2943 (11)	21 (13)	46 (9)	46 (9)	0	0	29 (27)	1	1
O(3)	24(m)	1104 (9)	1104 (9)	3405 (12)	74 (9)	74 (9)	48 (13)	54 (25)	45 (17)	45 (17)	1	1
Ag(1)	8(g)	1914 (2)	1914 (2(	1914 (2)	95 (10)	95 (10)	95 (10)	136 (5)	136 (5)	136 (5)	1	0.91 (1)
Ag(2)	6(e)	0	0	1709 (7)	10 (3)	10 (3)	8 (3)	0	0	0	1/3	0.35 (1)
Ag(3)	12(i)	0	4223 (24)	4223 (24)	394 (79)	321 (46)	321 (46)	0	0	−54 (102)	1/6	0.13 (1)

d. Crystal 4

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor fixed[d]	occupancy factor varied
(Si,Al)	24(k)	0	1824 (3)	3691 (3)	16 (2)	11 (3)	13 (2)	0	0	6 (4)	1[c]	1[c]
O(1)	12(h)	0	2080 (12)	1/2	7 (14)	5 (12)	13 (9)	0	0	0	1	1
O(2)	12(i)	0	2952 (7)	2952 (7)	34 (9)	24 (5)	24 (5)	0	0	9 (16)	1	1
O(3)	24(m)	1097 (6)	1097 (6)	3334 (8)	42 (5)	42 (5)	53 (9)	48 (13)	40 (9)	40 (9)	1	1
Ag(1)	8(g)	1907 (2)	1907 (2)	1907 (2)	96 (2)	96 (2)	96 (2)	148 (4)	148 (4)	148 (4)	1	1.00 (1)
Ag(2)	6(e)	0	0	1684 (3)	30 (1)	30 (1)	23 (3)	0	0	0	0.58	0.60 (1)
Ag(3)	24(m)	242 (16)	4356 (29)	4356 (29)	78 (213)	81 (36)	81 (36)	−17 (67)	−17 (67)	−15 (82)	0.02	.036 (3)

e. Crystal 5

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor
(Si,Al)	24(k)	0	1834 (5)	3693 (4)	17 (5)	16 (5)	7 (4)	0	0	1 (6)	1[c]
O(1)	12(h)	0	2093 (18)	1/2	64 (23)	43 (20)	27 (18)	0	0	0	1
O(2)	12(i)	0	2935 (12)	2935 (12)	31 (17)	24 (10)	24 (10)	0	0	30 (25)	1
O(3)	24(m)	1086 (9)	1086 (9)	3322 (11)	44 (9)	44 (9)	31 (12)	29 (21)	39 (15)	39 (15)	1
Ag(1)	8(g)	1891 (3)	1891 (3)	1891 (3)	86 (3)	86 (3)	86 (3)	130 (6)	130 (6)	130 (6)	0.97 (1)
Ag(2)	6(e)	0	0	1676 (6)	35 (4)	35 (4)	28 (7)	0	0	0	0.58 (1)

f. Crystal 6

atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	occupancy factor
(Si,Al)	24(k)	0	1834 (9)	3695 (8)	42 (9)	38 (10)	42 (10)	0	0	2 (15)	1[c]
O(1)	12(h)	0	1990 (23)	1/2	179 (53)	3 (29)	60 (38)	0	0	0	1
O(2)	12(i)	0	2924 (19)	2924 (19)	33 (31)	59 (21)	59 (21)	0	0	0 (61)	1
O(3)	24(m)	1074 (13)	1074 (13)	3288 (19)	99 (19)	99 (19)	97 (30)	90 (52)	−74 (36)	−74 (36)	1
Ag(1)	8(g)	1824 (71)	1824 (71)	1824 (71)	275 (13)	275 (13)	275 (13)	472 (25)	472 (25)	472 (25)	0.85 (2)
Ag(2)	6(e)	0	0	1652 (19)	56 (11)	56 (11)	250 (33)	0	0	0	0.41 (2)

[a] Positional and anisotropic parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Rms displacements can be calculated from β_{ii} values using the formula $\mu_i = 0.225a(\beta_{ii})^{1/2}$, where a is the cell constant (see Table I). [c] Occupancy for (Si) = ½; occupancy for (Al) = ½. [d] All crystallographic parameters and esd's, with the exception of those in the next (last) column, were calculated using these internally consistent occupancies.

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

	crystal 1	crystal 2	crystal 3	crystal 4	crystal 5	crystal 6
(Si,Al)-O(1)	1.619 (8)	1.647 (4)	1.641 (7)	1.639 (4)	1.636 (7)	1.60 (1)
(Si,Al)-O(2)	1.67 (1)	1.669 (8)	1.642 (15)	1.658 (10)	1.642 (15)	1.62 (2)
(Si,Al)-O(3)	1.68 (1)	1.672 (5)	1.670 (11)	1.677 (7)	1.683 (11)	1.67 (2)
Ag(1)-O(3)	2.24 (2)	2.308 (5)	2.311 (13)	2.249 (9)	2.247 (12)	2.20 (9)
Ag(2)-O(3)	2.83 (2)	2.815 (8)	2.835 (15)	2.785 (8)	2.765 (14)	2.71 (3)
Ag(3)-O(2)	2.65 (8)	2.44 (5)	2.22 (3)	2.46 (2)		
Ag(4)-O(1)		2.26 (4)				
Ag(5)-O(1)		2.871 (5)				
Ag(1)-Ag(2)	3.35 (1)	3.347 (5)	3.338 (3)	3.327 (2)	3.295 (3)	3.15 (8)
Ag(2)-Ag(2)	2.88 (1)	3.028 (9)	2.972 (8)	2.928 (4)	2.911 (7)	2.84 (3)
O(1)-(Si,Al)-O(2)	113 (1)	109.8 (5)	112.1 (9)	112.2 (6)	113.3 (9)	118 (1)
O(1)-(Si,Al)-O(3)	110 (1)	110.3 (4)	108.7 (9)	111.1 (6)	111.8 (8)	111 (1)
O(2)-(Si,Al)-O(3)	108 (1)	108.4 (4)	109.1 (7)	107.5 (5)	107.2 (7)	106 (1)
O(3)-(Si,Al)-O(3)	108 (1)	109.5 (10)	108.9 (10)	107.1 (5)	104.8 (9)	103 (2)
(Si,Al)-O(1)-(Si,Al)	160 (1)	152.1 (9)	155.8 (9)	157.9 (5)	157.5 (5)	166 (2)
(Si,Al)-O(2)-(Si,Al)	154 (1)	157.5 (4)	158.4 (10)	156.5 (7)	159.1 (10)	160 (1)
(Si,Al)-O(3)-(Si,Al)	141 (1)	144.6 (5)	146.6 (10)	142.1 (7)	142.4 (9)	141 (1)
O(3)-Ag(1)-O(3)	120 (1)	119.8 (4)	119.8 (7)	119.6 (4)	119.7 (6)	120 (4)
O(3)-Ag(2)-O(3)	57.6 (1)	58.0 (3)	57.3 (6)	58.0 (3)	57.6 (5)	57.5 (8)
Ag(1)-Ag(2)-Ag(1)	89.5 (5)	89.7 (4)	89.6 (2)	89.6 (1)	89.6 (2)	89.7 (2)

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding value.

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

	crystal 1	crystal 2	crystal 3	crystal 4	crystal 5	crystal 6
O(2)	0.275	0.207	0.195	0.265	0.266	0.289
Ag(1)	0.140	0.094	0.091	0.137	0.126	0.033
Ag(2)	−2.76	−2.760	−2.771	−2.729	−2.707	−2.654

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

0.109. The final difference syntheses showed three peaks at (0, 0, 0), (0.19, 0.19, 0.19), and (0.23, 0.23, 0.5) with peak heights of 1.8, 2.3, and 1.8 e Å^{-3} (esd = 0.2 e Å^{-3}). The second peak represents residual density from Ag(1), and the first and third peaks were not stable in least-squares refinement. See Tables I, IIc, III, and IV for additional information.

Crystal 4. Using the atomic coordinates from the structure of crystal 3, simultaneous occupancy, positional, and thermal parameter refinement was initiated. Anisotropic refinement of all positions converged quickly to $R_1 = 0.082$ and $R_2 = 0.072$. The number of Ag^+ ions at Ag(1), Ag(2), and Ag(3) (Table IId) refined to 7.98 (7), 3.59 (5), and 0.87 (6), respectively. These values were reset and fixed at 8, 3.5, and 0.5 silver atoms or ions, respectively, by the assumption of stoichiometry at Ag(1), and the need to locate 12 Ag species in the unit cell (because the crystal was not silvered). The final refinement converged at $R_1 = 0.083$ and $R_2 = 0.076$. A final difference Fourier synthesis was featureless except for two large but insignificant peaks at the origin (0, 0, 0; density = 3.5 e Å^{-3}) and on the threefold axis (x, x, x; $x = 0.125$, density = 3.5 e Å^{-3}). The latter was not stable in least-squares refinement. See Tables I, IId, III, and IV for additional information.

Crystal 5. Initial full-matrix least-squares refinement began with the same framework atomic parameters and silver positions as those found in crystal 4. Anisotropic refinement of all positions converged to the error indices $R_1 = 0.082$ and $R_2 = 0.081$. The Ag(3) position refined to an occupancy of zero in this structure. Simultaneous refinement of occupancy, positional, and anisotropic thermal parameters of Ag(1) and Ag(2) indicated 7.8 ions at Ag(1) and 3.5 atoms at Ag(2). When these values were reset and fixed at 8 Ag^+ at Ag(1) and 4 Ag^0 at Ag(2), the error indices converged to $R_1 = 0.094$ and $R_2 = 0.088$. A difference Fourier function revealed two peaks on the threefold axis (x, x, x) at $x = 0.088$ (density = 0.8 e Å^{-3}) and $x = 0.125$ (density = 3.4 e Å^{-3}). Both peaks were unstable in least-squares refinement. See Tables I, IIe, III, and IV for additional information.

Crystal 2. This crystal was exposed to 10 Torr of NO gas during data collection. The crystal structure indicated that no NO had been sorbed. Simultaneous least-squares refinement of occupancy, positional, and anisotropic thermal parameters taken from the structure of crystal 4 converged to $R_1 = 0.122$ and $R_2 = 0.135$. A difference Fourier synthesis revealed three peaks at (0.0, 0.406, 0.5), (0.414, 0.438, 0.438), and (0.234, 0.234, 0.5). The corresponding peak heights were 2.0–2.2 e Å^{-3}, esd = 0.2 e Å^{-3}. The second peak was not stable in refinement. Full-matrix least-squares refinement including the two other peaks converged at $R_1 = 0.077$ and $R_2 = 0.066$. Occupancy refinement indicated 8.0 atoms at Ag(1), 1.56 at Ag(2), 0.4 at Ag(3), 1.7 at Ag(4), and 0.3 at Ag(5). The final difference function was featureless except for a small origin peak (density = 2.4 e Å^{-3}, esd = 0.14 e Å^{-3} at a general position, and therefore the esd = (0.14)(48) = 6.7 e Å^{-3} at this special position).[30] See Tables I, IIb, III, and IV for additional information.

Crystal 6. Full-matrix least-squares refinement was initiated using the framework atomic parameters and the Ag(1) and Ag(2) positions from crystal 4. It converged to $R_1 = 0.163$ and $R_2 = 0.114$. Simultaneous refinement of occupancy, positional, and anisotropic thermal parameters indicated occupancies of 6.8 at Ag(1) and 2.4 at Ag(2). The largest peak in the final difference function was an insignificant one at the origin. The electron density function in the vicinity of the 8-rings was featureless. See Tables I, IIf, III, and IV for additional information.

Crystal 7. This crystal was subjected to a particularly strenuous heat treatment (see Table I). All reflections for which $-4 \leq h \leq 4$, $-4 \leq k \leq 4$, and $-4 \leq l \leq 4$ were examined. Of these, only eight unique reflections could be considered significant above background, after equivalent reflections were merged: (0, 0, 1), (0, 0, 3), (0, 1, 1), (0, 1, 4), (0, 2, 2), (1, 1, 1), (1, 1, 3), and (1, 2, 3). Only the scale factor and the occupancy numbers of Ag(1) and Ag(2) were refined, to give 2.2 silver atoms or ions at Ag(1) and 2.0 at Ag(2). All other positional and thermal parameters were fixed at the values found in the structure of crystal 4. The crystal, like crystal 6, was silver in color and its diffraction pattern indicated that silver powder and several moderately large silver crystals were present in addition to the zeolite crystal. The total diffracted intensity from silver appeared to be comparable to that from the zeolite.

All Crystals. The quantity minimized in least squares is $\Sigma w(F_o - |F_c|)^2$ and the weights (w) are the reciprocal squares of $\sigma(F_o)$, the standard deviation of each observed structure factor. Atomic scattering factors[31,32] for O^- and $(Si,Al)^{+1.75}$ (the average of Si^0, Si^{4+},

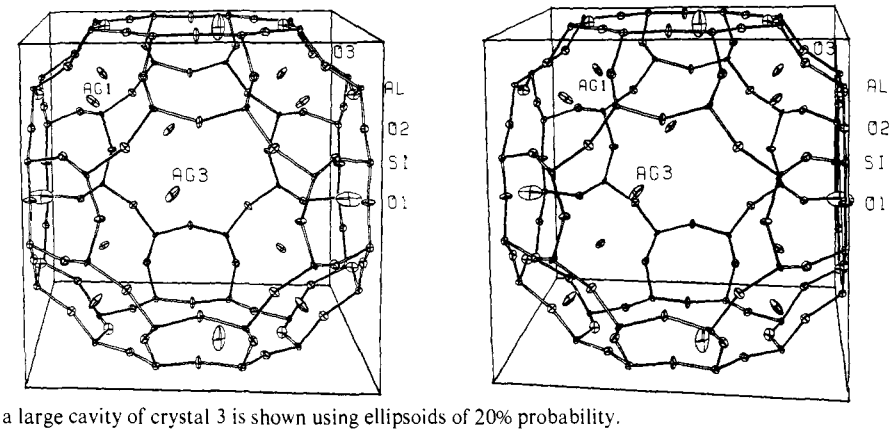


Figure 1. A stereoview of a large cavity of crystal 3 is shown using ellipsoids of 20% probability.

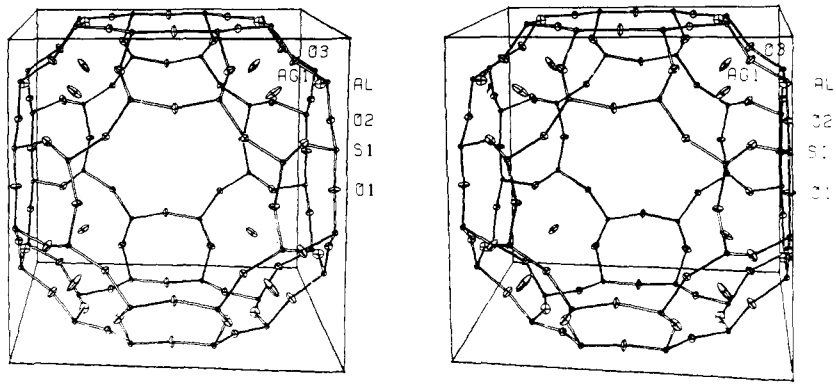


Figure 2. A stereoview of a large cavity of an idealized structure ($Ag^{+}_{8}Ag^{0}_{4}H^{+}_{2}Si_{12}Al_{12}O_{47}$) is shown using ellipsoids of 20% probability.

Al^0, and Al^{3+}) of the zeolite framework, and of Ag^+ were used. The scattering factors for $(Si,Al)^{+1.75}$, O^-, and Ag^+ were modified to account for the real components ($\Delta f''$) of the anomalous dispersion correction.[33]

Zeolite A is particularly suitable for crystallographic analysis, as compared to other zeolites, because its framework composition is stoichiometric, as is its initial Ag^+ content after complete ion exchange. This, and the relatively large number of silver atoms and ions in the structure, has allowed some crystallographic equipoints to be filled or stoichiometrically occupied. Structure solution has been very much facilitated by these considerations; hence the initial choice of zeolite A.

Listing of observed and calculated structure factors for all structures are given in Supplementary Tables I–VII; see paragraph at end of paper regarding supplementary material.

Discussion

Silver Ions and Clusters. When fully Ag^+-exchanged zeolite A[12] is dehydrated, each of its eight threefold-axis Ag^+ cations moves much closer to the centers of the 6-oxygen rings[13] (see Table IV), sites of near trigonal planar coordination. The remaining four Ag^+ ions would have been expected at sites like those found for cations in the structures of dehydrated Na_{12}-A,[15] Cs_7K_5-A,[16] K_{12}-A,[18] $Rb_{11}Na$-A,[19] or Tl_{12}-A.[20] Three would be associated with 8-rings, and the remaining one would be at a site of zero, or near zero, coordination, perhaps near a 4-ring.[13]

An Ag(2)–Ag(2) distance very nearly equal to the Ag–Ag distance in silver metal must exist whenever more than two silver atoms or ions are present at Ag(2) per unit cell. This many are certainly present in crystals 4 and 5. It follows that the position Ag(2) is occupied by a reduced silver species, probably neutral silver atoms. If this position were filled in a fraction of the sodalite units, closest packed clusters of six silver atoms would exist in all seven crystals. This hexasilver molecule would be octahedral and would show the full symmetry of its site, ${}^{4}_{m}\bar{3}^{2}_{m}(O_h)$ at the center of the sodalite unit.[34]

The distance between Ag(1) and its nearest framework oxide ions, at O(3), is short, ca. 2.25 Å. This indicates that the silver species at Ag(1) are the ions, Ag^+.

The distance between Ag(2) and its nearest framework oxide ions, again at O(3), is much longer, ca. 2.78 Å. This indicates that a reduced Ag^0 atom (an uncharged silver cluster) and not a Ag^+ ion (or a cluster with a formal charge) exists at Ag(2).

The distance between Ag(1) and Ag(2), 3.31 Å, is too short to be an unmoderated Ag^+–Ag^+ contact, and too long to be a Ag^0–Ag^0 bond. Accordingly and consistent with the previous two paragraphs, Ag(1)–Ag(2) must be an Ag^0–Ag^+ coordination contact distance. In further support of this are the small and nearly spherical thermal ellipsoids (B ca. 1.8 Å) observed for the atoms of the silver clusters in all structures, which indicate that these atoms are held firmly in place.

The two distances, Ag(1)–Ag(2) ca. 3.31 Å and Ag(2)–Ag(2) ca. 2.92 Å, show clearly that the bonding electron density is predominantly located on the central six silver atoms, although complexation requires that some of it be delocalized onto the Ag^+ ions at Ag(1). Thus it is inappropriate to discuss the result as a charged cluster whose formula would be Ag^{n+}_{6+n}, where n is 6 or 8, as is discussed later.

An interaction must also occur between each of the atoms of the clusters at Ag(2) and four equivalent framework oxide ions at O(3), the separation being ca. 2.78 Å. It is proposed that the silver atoms behave as weak Lewis acids with respect to the zeolite framework, accepting electron density and delocalizing it through the coordination interaction onto the ions at Ag(1). This Ag(2)–O(3) interaction must also contribute to the stabilization of the silver cluster within the zeolite, and to the small thermal motions of the silver atoms.

Without a mechanism for the stabilization of atoms or small neutral clusters within the zeolite, like that provided for the silver cluster by the ions at Ag(1) and O(3), metal atoms would

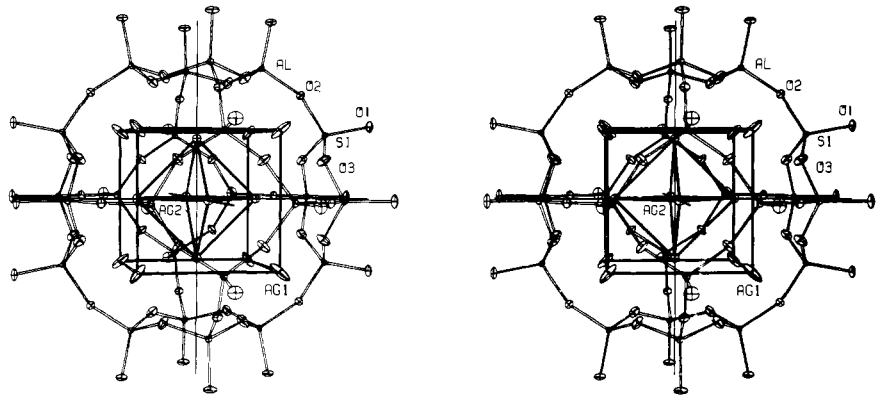


Figure 3. A stereoview of a sodalite unit containing an octahedral Ag_6 molecule within a cube of eight Ag^+ ions is shown using ellipsoids of 20% probability.

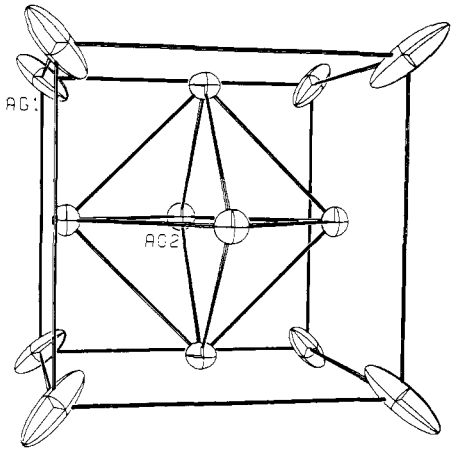


Figure 4. The octahedral Ag_6 molecule, stabilized by coordination to $8Ag^+$ ions is shown. Ellipsoids of 50% probability are used.

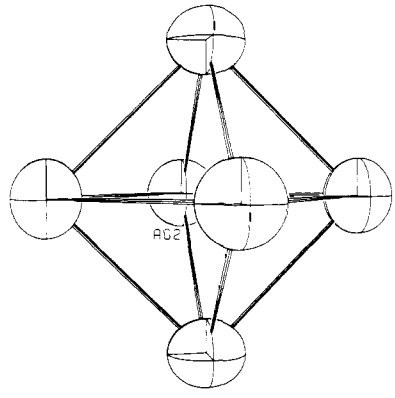


Figure 5. The octahedral Ag_6 molecule is shown using ellipsoids of 99% probability.

generally not be retained within the zeolite structure. Because this mechanism is in operation, it is reasonable to accept, as has been shown crystallographically, that atoms of silver have formed within the zeolite under conditions milder than those needed to observe the accretion of silver metal on the surface of the zeolite crystal.

Crystals 4 and 5 of Table I have the approximate stoichiometry $Ag^+{}_8Ag^0{}_4H^+{}_{2x}Si_{12}Al_{12}O_{46+x}$, $x \simeq 1$, per unit cell. These have the highest concentrations of silver atoms encountered in this work. With this stoichiometry, one-third of the sodalite units are empty of silver clusters. The remaining two-thirds each contain a cluster of six silver atoms arranged in the form of a perfect octahedron, at the center of the sodalite unit, and in an orientation which is fully consistent with the symmetry of its environment. The eight Ag^+ ions per unit cell lie on the threefold axes of the Ag_6 cluster (see Figures 3, 4, and 5). Each Ag^+ ion is ca. 3,31 Å from three Ag atoms. The Ag-Ag distance in the cluster, 2.92 Å, is slightly more than the Ag-Ag distance in silver metal, 2.89 Å.[35] The six-atom cluster shown in Figure 5 is closest packed, and is like a unit of the structure of silver metal, which is cubic closest packed. It also has the natural growth form {111} of silver metal. *It is the smallest possible fully developed single crystal of silver.*

Arguments have been presented which indicate that all of the silver clusters in the structures of crystals 4 and 5 are six atoms in size.[25,34] However, the continuum of stoichiometries presented in Table I prove only that the largest clusters cannot be smaller than four silver atoms in size. It is also possible that a distribution of cluster sizes exists within the zeolite, although the small and nearly spherical thermal ellipsoid at the Ag(2) position argues strongly that all clusters in all structures are identical, except for subtle variations in Ag-Ag bond lengths.

The study of crystal 7 shows that the number of Ag^+ ions at Ag(1) is approximately equal to the number of silver atoms at Ag(2) in that crystal (see Table I). This indicates that the formula of the silver complex in that crystal is $(Ag^+)_n(Ag_m)$ with $m = 6$, probably, according to the arguments persented herein and before,[25] and with $n = 6$ or 8 (arguments favoring $n = 8$ follow shortly). It remains possible that the formula $(Ag^+)_6(Ag_6)$ applies to all crystals—that the eight ions at Ag(1) can be of two kinds, six closer to the Ag_6 molecule and two farther away. Although the elongated thermal ellipsoid for the ions at Ag(1) allows for this possibility, it could not be established in trial least-squares refinements. The elongation of the thermal ellipsoids of the ions at Ag(1) does not appear to correlate with the number of reduced silver atoms per unit cell, arguing that such a division of Ag(1) ions into two kinds is not appropriate, and that the formula of the complex is $(Ag^+)_8(Ag_6)$ when a sufficient number of Ag^+ ions are available.

Upon heating from 2 to 10 days at constant temperatures ranging from 395 to 450 °C (see Table I), a progressive reduction of the 4-ring and 8-ring Ag^+ ions is observed; 6-ring Ag^+ ions are not reduced. The Ag^+ ions at Ag(3) and Ag(4) are associated with 8-ring oxygens (see Figure 2), and their relatively large thermal parameters indicate that they are loosely bound to the zeolite framework, and therefore that their coordination environments are relatively unsatisfactory. The Ag^+ ion at Ag(5) is statistically distributed over a 12-fold equipoint in the large cavity on a twofold axis opposite a 4-ring. It appears to be the least favorable position because its approaches to framework oxide ions are the longest (Ag(5)-O(1)

= 2.87 Å and Ag(5)-O(3) = 2.90 Å) and because its anisotropic thermal parameter is large. Thus, the Ag^+ positions which are associated with 4-ring and 8-ring oxygens are the first to be depleted because they are the least satisfactorily coordinated within the zeolite. It is because only four such Ag^+ ions are initially present per unit cell, in part, that the state of two-thirds occupancy of hexasilver molecules is an apparent end point.

Reduction of Ag^+ by Oxide Ions. The reduction of Ag^+ to Ag^0 proceeds by two separate processes. Initially it is oxide ions of residual water molecules which are reduced to oxygen gas, leaving H^+ ions.[36,37] This reaction and its extent per unit cell is approximately

$$Ag^+{}_{12}Si_{12}Al_{12}O_{48}\cdot 3H_2O \rightarrow Ag^0{}_2Ag^+{}_{10}H^+{}_2Si_{12}Al_{12}O_{48} + \tfrac{1}{2}O_2 + 2H_2O$$

About one-third of the water molecules which remained per unit cell after an initial vacuum-dehydration procedure at 350 °C have reacted with Ag^+ ions. The remainder have been removed without reaction to leave the zeolite fully dehydrated. The oxide ions of the zeolite framework have not been involved so the zeolite framework remains undamaged, and its single-crystal diffraction pattern remains very detailed. Perhaps the following reactions occur within the sodalite unit

$$Ag_3(H_2O)_3{}^{3+} \rightarrow Ag^+ + Ag_2(H_2O)^{2+} + 2H_2O$$

which would simply be a continuation of the dehydration process,[12] followed by

$$Ag_2(H_2O)^{2+} \rightarrow 2H^+ + 2Ag + \tfrac{1}{2}O_2$$

By this reaction, which decreases the number of Ag^+ ions in the unit cell, the noble element silver avoids the dilemma of being in an oxidized state (as Ag^+) without being stabilized by a suitable coordination environment.

After the supply of water molecules is depleted and the zeolite is fully dehydrated, additional Ag^+ ions can be reduced by oxide ions of the zeolite framework according to the unit cell reaction

$$Ag^0{}_2Ag^+{}_{10}H^+{}_2Si_{12}Al_{12}O_{48} \rightarrow Ag^0{}_4Ag^+{}_8H^+{}_2Si_{12}Al_{12}O_{47} + \tfrac{1}{2}O_2$$

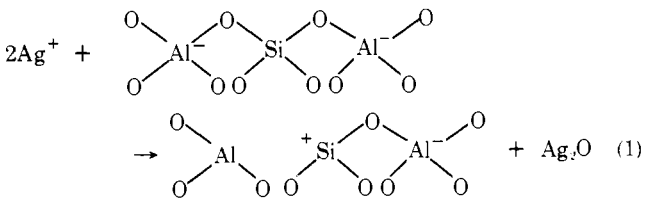
As this reaction proceeds, the single crystal diffraction pattern begins to deteriorate, indicating that the zeolite framework itself is being damaged. When the reaction is completed at about 425 °C, the three ions at 8-ring sites and the one near zero coordinate Ag^+ ion opposite a 4-ring (all but the eight most satisfactorily coordinated 6-ring Ag^+ ions) have been reduced. This is the source of the maximum number of silver atoms to be observed per unit cell in the seven structures studied.

When the heating under vacuum is carried out for longer times or at higher temperatures, the reduction proceeds further and includes the 6-ring Ag^+ ions. However, it is by coordination to these that hexasilver is stabilized within the zeolite. It is observed that when the number of Ag^+ ions per unit cell decreases below eight at temperatures greater than about 450 °C, crystallites of silver metal form at the surface of the zeolite. Some silver atoms remain within the zeolite, however, in numbers related (but not in a simple way) to the number of Ag^+ ions in the structure. The tendency of Ag^+ ions to distribute themselves evenly among the unit cells is modified by the stabilization of eight Ag^+ ions at some sodalite units by Ag_6. The only silver atoms to leave the zeolite appear to be those which are in excess with respect to the stoichiometry $(Ag^+)_8(Ag_6)$ in some sodalite units at ca. 450 °C. At 25 °C, six Ag^+ ions suffice to contain the hexasilver molecules,[25] and the formula of the complex can be $(Ag^+)_6(Ag_6)$. The zeolite crystal continues to deteriorate, and the cell constant to decrease (Table I), as the reduction proceeds toward completion, and as more framework oxygen is lost. In crystal 7, whose silver content is only about two atoms and two ions per unit cell (Table I), so that 10 of the 12 Ag^+ ions have been reduced, the cell constant has decreased dramatically from about 12.30 to 11.42 Å.

When all Ag^+ ions are reduced, the unit cell composition would become $Si_{12}Al_{12}O_{42}$ or $H_2Si_{12}Al_{12}O_{43}$, three molecules of O_2 would have been released, and 12 silver atoms would have left the zeolite structure. Perhaps a few features of the single crystal diffraction pattern would remain which would allow the material to be identified as a modified form of zeolite A.

Recently Jacobs[38] found, by volumetric methods, that the dehydration of Ag_{12}-A at 390 °C for a period of about 1 day released 0.25 molecules of O_2, corresponding to the reduction of one Ag^+ ion, per unit cell. This result is consistent with the work reported herein, that upon heating at higher temperatures for longer times, the reaction has proceeded to various greater extents, some nearing completion.

The second and principal mechanism may be that proposed by Tsutsumi and Takahashi,[6] who prepared silver metal external to the structure of Ag^+-exchanged zeolite Y by heating to 600 °C in flowing helium gas (eq 1) followed by $Ag_2O \rightarrow 2Ag^0 + \tfrac{1}{2}O_2$.



Jacobs et al.[39] reported that a similar process occurs in partially Cu(II)-exchanged Na-Y. The following equilibrium involving zeolite oxide ions was confirmed by various physical methods, including mass spectrometric identification of labeled O_2.

$$4Cu^{2+} + 2O^{2-} \rightleftharpoons 4Cu^+ + O_2$$

Copper is less noble than silver, and its reduction does not proceed as easily upon simply heating the dehydrated zeolite.

The principle of local electrical neutrality suggests that as 8-ring Ag^+ ions are progressively reduced, 8-ring oxide ions (O(1), O(2), or both) should be progressively removed (oxidized). Furthermore, the O(1) oxide ions are components of the small cubes,[13] which are relatively strained and unstable, and uncommon in aluminosilicate systems, while the O(2) oxide ions are components of the more stable and more common sodalite units. (The small systematic increase in the O(1) thermal parameter which might be expected is not observed because of their high esd's and because these parameters fluctuate from structure to structure in response to variations in the framework conformation.) This indicates that it is O(1) oxide ions which are removed from the zeolite framework while the O(2) oxide ions remain in the coordination spheres of the three-coordinate (Si,Al) ions. In support of this conclusion, the shortest Ag^+-O^{2-} distance observed among these structures is the 2.26 (4) Å Ag(4)-O(1) approach in crystal 2; the Ag^+ ion which is most easily reduced is interacting strongly with O(1), suggesting that it is the oxide ions at O(1) which are oxidized. This conclusion is supported by the study of dehydrated $Ag_{6.5}Tl_{5.5}$-A.[40] For the first six crystals, no more than two-thirds of the zeolite cubes have lost an oxide ion. In crystal 7, 6-ring Ag^+ ions have been reduced, so it may be true that some oxide ions at O(3) or O(2) have been oxidized.

As 8-ring Ag^+ ions are lost, the (Si,Al)-O distances in that ring decrease (Table III, rows 1 and 2). This appears to be a

result of the decrease in the average coordination number for the ions at O(1) and O(2), from >2 to 2.

Recently, dehydrated crystals of Ag_{12}-A treated with hydrogen at 24 and 150 °C were studied.[41] In each case, the zeolite's diffraction pattern was lost; only powder diffraction lines from small crystals of silver metal could be observed. A third crystal was dehydrated in oxygen gas at 400 °C, exposed to hydrogen at 330 °C, and treated with oxygen at 330 °C. This time the diffraction pattern was quite good, indicating that this crystal, which had been damaged and which had lost silver initially, had repaired itself and had reabsorbed silver during the final oxygen treatment. The resulting black-brown crystal contained 11 Ag^+ ions and approximately 0.56 Ag^0 atoms per unit cell. The color of the crystal indicates that it is coated with Ag_2O, to account for the remaining 0.44 silver species. This shows that the zeolite repair occurs only to a limited extent, only while suitable lattice sites are available for the newly oxidized Ag^+ ions. After eight Ag^+ ions locate in 6-rings and three in 8-rings, filling those positions, the remaining site, which would be opposite a 4-ring or at another near zero or zero coordinate position, is not filled, even though silver atoms, oxygen gas, and H^+ ions coexist at 330 °C.

Such a repair process is unusual in crystallography. Its occurrence is even more remarkable because the dehydrated zeolite is not a thermodynamically stable phase—the silicate β-cristobalite[23,42] should be one of the stable phases under the conditions employed. However, this repair appears more reasonable in view of the tentative conclusions of the preceding paragraph, that large blocks of the structure, the 60-atom sodalite units (exclusive of silver atoms and ions), perhaps, have survived the decomposition intact. These units would retain their positions and approximate orientations, and would need only to be reconnected to restore the integrity of the single crystal. Actually, whichever four moderately well distributed oxide ions of the 48 present were lost, sufficient rigidity is likely to remain to preserve the general order of the structure, so that the repair process could be facile.

Other Discussion. The yellow color of all nonsilvered crystals is attributed to a charge transfer interaction between the Ag^+ ions at Ag(1) and the oxide ions at O(3). The distance between an ion at Ag(1) and its three nearest 6-ring oxygen neighbors is fairly short, 2.25-2.31 Å, compared to the sum of the Ag^+ and O^{2-} radii, 2.58 Å[43] (see Table III). It has been proposed[44] that as the Ag-O bonds in a compound become shorter and more covalent, a color, initially yellow for Ag_3PO_4 (Ag-O = 2.34 Å) and Ag_2CO_3 (Ag-O = 2.30 Å), appears. Ag_2O, in which Ag-O = 2.05 Å, is brown-black. Where longer Ag-O bonds are found, the compounds are colorless, e.g., hydrated Ag_{12}-A (2.40 Å),[12] $AgNO_3$ (2.48 Å),[45] Ag_2SO_4 (2.50 Å),[46] and $AgClO_3$ (2.51 Å).[47] The corresponding Ag-O distance in dehydrated fully Ag^+-exchanged zeolite Y is 2.32 Å,[48] approximately the same as that reported in this work. Although its color was not reported, it would have been expected to be lighter, perhaps colorless, because the silicate-rich zeolite Y would be a poorer base.

It is obvious that silver atoms have migrated out of the structures of silver-colored zeolite crystals. The rotation pictures of those crystals always showed silver (1, 1, 1) and (0, 0, 2) powder diffraction lines; occasionally additional silver lines could be seen.

The $(Ag^+)_6(Ag_6)$ cluster has been found within the sodalite units of an ethylene sorption complex of partially decomposed fully Ag^+-exchanged zeolite A.[25] The remaining threefold-axis Ag^+ ions, and perhaps those in the 8-rings, have each been complexed by one C_2H_4 molecule. By this process, ethylene acts as a titrating agent to count the number of Ag^+ ions per unit cell which are not strongly coordinated to hexasilver. Ethylene does not displace the Ag_6 cluster as a ligand to six Ag^+ ions, whereas NH_3 in forming N_3H_3 and N_3H_5 does.[2] This indicates that the ligand strength of Ag_6 is between those of ethylene and the triazanes with respect to Ag^+. Of course, this conclusion is strictly valid only for the coordination numbers and geometries involved.

The occupancy numbers of the Ag^+ ions in crystal 1 are lower than would be expected in view of the relatively mild dehydration conditions employed, and the crystal silvered prematurely. This occurred because trace amounts of methylamine sorbed onto some zeolite beads were present by mistake in the vacuum system. Reducing vapors from this source expedited the reduction of Ag^+ in this and several other preparations. However, the structure of crystal 1 is included in this report because it is otherwise consistent with those of the other crystals (see Table III).

As the dehydrating temperature is increased and the dehydrating period lengthened, the Ag(2)-Ag(2) distances in the silver cluster decrease, as do the Ag(1)-Ag(2) coordination distances. Perhaps, as the anionic charge of the zeolite framework decreases owing to the loss of oxide ions, the complexed hexasilver clusters can shrink away from it, toward their own centers. On this basis, it can be expected that the Ag-Ag bond length in an isolated hexasilver molecule would be less than that in the bulk metal.

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Supplementary Material Available: Listings of the observed and calculated structure factors (Supplementary Tables I-VII) (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) P. A. Kilty and W. M. H. Sachtler, *Catal. Rev.*, **4**, 27 (1970).
(2) Y. Kim, J. Gilje, and K. Seff, *J. Am. Chem. Soc.*, **99**, 7057 (1977).
(3) J. A. Rabo, C. L. Angell, P. H. Kasai, and V. Schomaker, *Discuss. Faraday Soc.*, **41**, 328 (1966).
(4) C. M. Naccache and Y. Ben Taarit, *J. Catal.*, **22**, 171 (1971).
(5) D. J. C. Yates, *J. Phys. Chem.*, **69**, 1676 (1965).
(6) K. Tsutsumi and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **45**, 2332 (1972).
(7) Y. Y. Huang, *J. Catal.*, **32**, 482 (1974).
(8) S. Matsumoto, M. Nitta, K. Ogawa, and K. Aomura, *Bull. Chem. Soc. Jpn.*, **48**, 1169 (1975).
(9) This nomenclature refers to the contents of the unit cell. For example, Na_{12}-A represents $Na_{12}Al_{12}Si_{12}O_{48}$, exclusive of water molecules if a hydrated crystal is considered.
(10) H. Beyer, private communication, 1977.
(11) H. Beyer, P. A. Jacobs, and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, **72**, 674 (1976).
(12) Y. Kim and K. Seff, *J. Phys. Chem.*, **82**, 1071 (1978).
(13) A discussion of zeolite nomenclature is available: (a) R. Y. Yanagida, A. A. Amaro, and K. Seff, *J. Phys. Chem.*, **77**, 805 (1973); (b) L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, **82**, 1041 (1960); (c) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).
(14) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 4039 (1977).
(15) V. Subramanian and K. Seff, *J. Phys. Chem.*, **81**, 2249 (1977).
(16) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 7059 (1977).
(17) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **100**, 3091 (1978).
(18) P. C. W. Leung, K. B. Kunz, and K. Seff, *J. Phys. Chem.*, **79**, 2157 (1975).
(19) (a) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **98**, 5031 (1976); (b) *ibid.*, **99**, 1112 (1977).
(20) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 6249 (1977).
(21) L. B. McCusker and K. Seff, *J. Am. Chem. Soc.*, **100**, 5052 (1978).
(22) J. F. Charnell, *J. Cryst. Growth*, **8**, 291 (1971).
(23) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed, and T. L. Thomas, *J. Am. Chem. Soc.*, **78**, 5963 (1956).
(24) H. S. Sherry, *J. Phys. Chem.*, **71**, 1457 (1967).
(25) Y. Kim and K. Seff, *J. Am. Chem. Soc.*, **100**, 175 (1978).
(26) K. Seff, *J. Phys. Chem.*, **76**, 2601 (1972).
(27) P. E. Riley, K. Seff, and D. P. Shoemaker, *J. Phys. Chem.*, **76**, 2593 (1972).
(28) Principal computer programs used in this study: T. Ottersen, COMPARE data reduction program, University of Hawaii, 1973: full-matrix least squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317 (revised 1976); Fourier program, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971; C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(29) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).
(30) D. W. J. Cruickshank, *Acta Crystallogr.*, **2**, 65 (1949).
(31) "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 73-86.

(32) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(33) Reference 31, pp 149–150.
(34) Y. Kim and K. Seff, *J. Am. Chem. Soc.*, **99**, 7055 (1977).
(35) "Handbook of Chemistry and Physics", 55th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1974, p F-201.
(36) Y. Kim and K. Seff, *J. Am. Chem. Soc.*, **100**, 3801 (1978).
(37) Y. Kim and K. Seff, *J. Phys. Chem.*, **82**, 925 (1978).
(38) P. A. Jacobs, private communication, 1977.
(39) P. A. Jacobs, M. Tielen, J.-P. Lihart, and J. B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, **72**, 2793 (1976).
(40) Y. Kim and K. Seff, *J. Phys. Chem.*, **82**, 1307 (1978).
(41) Y. Kim and K. Seff, *J. Phys. Chem.*, **82**, 921 (1978).
(42) R. M. Barrer and D. A. Langler, *J. Chem. Soc.*, 3804 (1956).
(43) Reference 35, p F-198.
(44) A. F. Wells, "Structural Inorganic Chemistry", Pergamon Press, Oxford, 1967, p 267.
(45) P. E. Lindley and P. Woodward, *J. Chem. Soc.*, 123 (1966).
(46) J. Donohue and L. Helmholz, *J. Am. Chem. Soc.*, **66**, 295 (1944).
(47) I. Naray-Sazbó and J. Pocza, *Z. Kirstallogr., Kristallgeom., Kristallphys., Kristallchem.*, **104**, 28 (1942).
(48) G. R. Eulenberger, D. P. Shoemaker, and J. G. Keil, *J. Phys. Chem.*, **71**, 1812 (1967).

Crystal Structures of Cyclopropane Complexes of Cobalt(II) and Manganese(II) in Partially Exchanged Zeolite A

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Abstract: The crystal structures of the cyclopropane sorption complexes of partially Co(II)-exchanged and partially Mn(II)-exchanged zeolite A have been determined using X-ray diffraction data collected by counter methods. Both structures were solved and refined in the cubic space group *Pm3m;* at 26 (1)°, the unit cell constants are 12.147 (2) Å for $Co_4Na_4Si_{12}Al_{12}O_{48}\cdot 4C_3H_6$ (unit cell stoichiometry) and 12.146 (4) Å for $Mn_4Na_4Si_{12}Al_{12}O_{48}\cdot 4C_3H_6$. Both complexes were prepared by dehydration at 350 °C and 1×10^{-5} Torr for 48 h, followed by exposure to cyclopropane gas at approximately atmospheric pressure. In each structure, the transition metal cations are located on threefold axes inside the large cavity, close to three trigonally arranged framework oxide ions on alternate 6-oxygen rings. The metal to oxygen distances are Co(II)–O = 2.174 (7) Å and Mn(II)–O = 2.122 (8) Å. Each of the four cyclopropane molecules in each structure is found to complex to a transition metal ion with Co(II)–C = 2.81 (7) Å and Mn(II)–C = 3.09 (6) Å. The threefold axes of the zeolite and of the sorbed molecules coincide, so that all carbon atoms in each cyclopropane molecule are equivalent and equidistant from the transition metal cation with which they are associated. In both cases, the cyclopropane molecules are loosely bound to the metal ions by a π ion to induced dipole interaction, a conclusion based on the long metal to carbon approach distances and the large anisotropic carbon thermal parameters. No interaction between Na^+ ions and cyclopropane molecules is observed. Full-matrix least-squares refinement converged to weighted R indices of 0.065 for the Co(II) complex and 0.083 for the Mn(II) complex, using the 373 and 331 reflections, respectively, for which $I_o > 3\sigma(I_o)$.

Introduction

Transition metal ions which have been ion exchanged into zeolites are generally unusually coordinated or coordinately unsaturated. As a result, they have unusual chemical properties. The zeolite framework, in contrast to conventional complexing ligands, does not conform to the geometrical requirements of the metal ions to form stable complexes. Rather, the metal ions must situate themselves in the most suitable of the various unsuitable sites available, using water or guest molecules if available, to achieve a relatively stable coordination environment. Upon dehydration, coordinative unsaturation appears or is very much enhanced.

For example, in hydrated partially Mn(II)-exchanged zeolite A, all Mn(II) ions are found to have nearly regular trigonal-bipyramidal coordination, with water molecules in the axial positions and three equivalent framework oxygen atoms arranged equatorially.[1] Upon dehydration, the Mn(II) ions are found to be three coordinate, with a near trigonal-planar geometry.[1] Co(II) ions have nearly the same trigonal-planar coordination[2] in dehydrated partially Co(II)-exchanged zeolite A.

Three-coordinate transition metal ions are unusual, and should tend to increase their coordination numbers by forming complexes with a large variety of ligand molecules, including some which are very poor Lewis bases indeed and are not commonly thought of as ligands at all. By vacuum methods and by using a zeolite, it is possible to study these ions without the interference of competing ligands from a solvent or from the atmosphere.

In order to characterize the activity of transition metal ions in the zeolitic environment, several structural studies of sorption complexes of zeolite A have been carried out by diffraction methods. The structures of the complex of Mn(II) with C_2H_2,[3] and those of Co(II) with CO, C_2H_2, C_2H_4, NO, NO_2, and Cl_2, have been determined.[2-6] Similarly, the complexes of Ag(I) with N_3H_3,[7] N_3H_5,[7] C_2H_4,[8] Cl_2,[9] and Br_2[10] have been reported. The structures of the sorption complexes of Cl_2 and O_2 with dehydrated Eu(II)-exchanged zeolite A have also been determined;[11,12] these show that oxidative addition has occurred to give Eu(IV), a new oxidation state for this element.

As a continuation of this work, cyclopropane was sorbed into dehydrated partially Co(II)- or Mn(II)-exchanged zeolite A. Nuclear quadrupole resonance[13] studies of C_3H_6 indicate that all of the carbon atoms in the cyclopropane molecules are sp^2 hybridized. This is further evidenced by the marked resemblance between cyclopropane and olefinic bond reactions.[14] Hence cyclopropane has some π character by which it might interact with transition metal cations. It has been found that cyclopropane sorbed by partially Ni(II)-exchanged zeolite A complexes with Ni(II) ions.[15] It is reasonable, therefore, to expect that similar complexes would form in the Co(II) and Mn(II) systems. The work was initiated to learn the detailed geometry of the cyclopropane complexes.

Experimental Section

Single crystals of the synthetic molecular sieve sodium zeolite 4A, stoichiometry $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$, were prepared by Charnell's

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