

increase is reflected in the shift of the MLCT band ($\text{Ru}^{\text{II}} \rightarrow \text{L}$) to lower energy than the monomeric or [II, L, II] cases (Tables II and VIII). A rough estimate of the increased stability of the MV state can be obtained from the observed MLCT band shifts. For example, if $\beta_1 = 8 \times 10^3 \text{ cm}^{-1}$ and Δ shifts from 20×10^3 to $19 \times 10^3 \text{ cm}^{-1}$ ΔE° will include perhaps 40 mV due to the π acidity effect. The estimate is made via eq 9 and assumes double occupancy of the relevant metal donor orbital.

(4) **Interactions in the [III, L, III] or [II, L, II] States.** For larger bridges, this should not be a factor. A direct test is the comparison of the MLCT band energies and shapes for the monomers and the fully reduced dimers [II, L, II]. The absence of significant changes indicates little instability in the [II, L, II] state. For smaller bridges, the balance of interelectronic repulsions on the metals and bridge with the stability due to $\pi\text{d}-\pi^*$ or $\pi\text{d}-\pi$ delocalization is difficult to quantify. The use of CT energies would be misleading in those cases since the mere presence of a metal center near the optical origin will perturb the band energy and shape.

(5) **Structural Distortion.** For bridging ligands studied here, the influence of the oxidation state of one metal center on the bonding at the other site is expected to be small. That is, the M-L bond lengths and angles in the MV state will be close to those found for normal Ru^{II} and Ru^{III} bonds.^{82,83} Therefore, it is not expected that geometric distortion will be important here. When the coordination spheres for the two metal centers overlap, structural distortion can be an important factor in determining K_c .

Conclusions

The mixed-valence complexes chosen for this study serve to illustrate several aspects of the effect of bridging ligand structure

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on metal-metal interactions in polymetallic systems. Since the auxiliary ligand ammonia is innocent with respect to the πd orbitals, the observed trends are known to be associated almost completely with variations in the bridging groups. The trends are predicted theoretically in a straightforward way by combining a molecular orbital description of the bridging ligand with a semiempirical measure of metal-ligand charge-transfer interactions. While the perturbational approach is satisfactory for localized MV complexes, it is not applicable for very strongly interacting or delocalized cases. The relationship of bridging ligand size, orientation of substituents, interplanar distances, and saturation to metal-metal interaction has been demonstrated both theoretically and experimentally. Bridging ligand effects in intramolecular electron transfer reactions can be related to the present work via the interaction parameter V_{AB} .

Although the complexes studied here represent only one type of bridged MV system, many of the general ideas advanced can be applied to other related phenomena. For example, the question of the mechanism of electronic conduction in biological redox reactions is clearly open to the type of analysis used here. As more experimental data on redox reactions involving structurally characterized metalloproteins and model systems becomes available, possible redox "pathways" can be evaluated.

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Registry No. $[\text{Ru}(\text{NH}_3)_5\text{pym}](\text{PF}_6)_2$, 83708-86-5; $[\text{Ru}(\text{NH}_3)_5]_2\text{pym}(\text{PF}_6)_4$, 83664-65-7; $[\text{Ru}(\text{NH}_3)_5]_2\text{pym}[\text{Cl}_6]$, 83664-66-8; $[\text{Ru}(\text{NH}_3)_5]_2\text{3CP}(\text{PF}_6)_4$, 83664-68-0; $[\text{Ru}(\text{NH}_3)_5]_2\text{4CP}(\text{ClO}_4)_4$, 83664-70-4; $[\text{Ru}(\text{NH}_3)_5]_2\text{2DCB}[\text{Br}_4]$, 83664-71-5; $[\text{Ru}(\text{NH}_3)_5]_2\text{13DCB}(\text{ClO}_4)_4$, 83664-73-7; $[\text{Ru}(\text{NH}_3)_5]_2\text{13DDB}(\text{BF}_4)_4$, 83664-74-8; $[\text{Ru}(\text{NH}_3)_5]_2\text{14DCB}(\text{CF}_3\text{SO}_3)_4$, 83664-75-9; $[\text{Ru}(\text{NH}_3)_5]_2\text{15DCN}(\text{ClO}_4)_4$, 83664-76-0; $[\text{Ru}(\text{NH}_3)_5]_2\text{16DCN}(\text{ClO}_4)_4$, 83664-78-2; $[\text{Ru}(\text{NH}_3)_5]_2\text{17DCN}(\text{ClO}_4)_4$, 83664-80-6; $[\text{Ru}(\text{NH}_3)_5]_2\text{26DCN}(\text{ClO}_4)_4$, 83664-82-8; $[\text{Ru}(\text{NH}_3)_5]_2\text{27DCN}[\text{I}_4]$, 83664-83-9; $[\text{Ru}(\text{NH}_3)_5]_2\text{13DCA}(\text{ClO}_4)_4$, 83664-85-1; $[\text{Ru}(\text{NH}_3)_5]_2\text{PPDCP}[\text{Br}_4]$, 83664-86-2.

Crystal Structure of Vacuum-Dehydrated Silver Hydrogen Zeolite A

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Contribution from the Centrum voor Oppervlaktescheikunde en Colloidale Scheikunde, B-3030 Leuven (Heverlee), Belgium, and the Department of the Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637. Received April 23, 1982

Abstract: Crystals of zeolite 4A were fully exchanged with AgNO_3 solution and immersed in NH_4OH solution for 65 h. Electron microprobe analysis gave $\text{Ag}_{70}\text{Si}_{96}\text{Al}_{96}\text{O}_{384} \cdot x\text{H}_2\text{O}$, but the numbers are imprecise because of inadequate standards. A total of 26 H atoms would be needed for charge balance with 96 Al atoms. X-ray diffraction data for a crystal dehydrated at 410 °C and 10^{-5} torr were refined in space group $Fm\bar{3}c$ ($a = 24.55 \text{ \AA}$). The mean T-O distances (1.598 and 1.729 Å) are consistent with earlier evidence for alternation of tetrahedra populated by Si and $\text{Al}_{0.5}\text{Si}_{0.5}$. A total of 66 Ag atoms were located in four sites: 44 Ag(2) atoms near the center of a 6-ring, and bonded to 3 O(3) atoms at 2.28 Å; 7 Ag(3) atoms displaced from the center of an 8-ring and bonded to three oxygens at 2.4-2.9 Å; 6 Ag(1) atoms opposite a 4-ring inside the sodalite unit at 2.82 Å from 4 O(3) atoms; 9 Ag(2') atoms displaced 0.5 Å from Ag(2) into the sodalite unit. The shortness of distances (2.95 and 2.92 Å) from Ag(1) to another Ag(1) and to Ag(2') supports earlier evidence for the presence of a neutral or nearly neutral Ag atom at site 1. However, the size of possible clusters cannot be inferred because only one in eight of the type 1 sites is occupied. Electron density at the center of the sodalite unit would correspond to 0.9 Al atom, but the density for the corresponding oxygen was not located.

Introduction

Although the aluminosilicate framework of Al-rich zeolites collapses if complete hydrogen exchange is attempted,¹ partial exchange can be achieved in several ways. Heating after partial

exchange with NH_4 results in liberation of NH_3 and formation of hydroxyl groups in the framework; however, vacuum extraction at 25 °C allowed dehydration without removal of NH_3 .² An ion exclusion effect³ allows replacement of Ag^+ by H^+ ; thus a single

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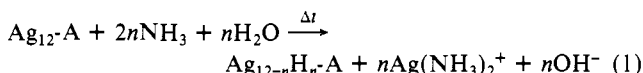
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Table I. Positional, Thermal,^a and Occupancy Factors of Dehydrated Ag_{12-n}H_n-A^b

	wyckoff position	x	y	z	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃	population
Si	96(i)	0.0	0.0931 (1)	0.1843 (2)	77 (7)	64 (6)	57 (7)	0	0	12 (5)	96.0
Al	96(i)	0.0	0.1862 (2)	0.0904 (2)	77 (7)	60 (8)	78 (8)	0	0	7 (5)	96.0
O(1)	96(i)	0.0	0.1090 (2)	0.2466 (4)	175 (10)	186 (11)	56 (10)	0	0	-2 (20)	96.0
O(2)	96(i)	0.0	0.1468 (4)	0.1487 (4)	154 (9)	119 (25)	70 (22)	0	0	40 (7)	96.0
O(3)	192(j)	0.0532 (2)	0.0577 (3)	0.1687 (1)	115 (15)	119 (15)	139 (6)	40 (6)	19 (10)	13 (10)	192.0
Ag(1)	48(e)	0.0849 (2)	0.0	0.0	101 (12)	130 (33)	98 (30)	0.0	0.0	0.0	5.7 (1)
Ag(2)	64(g)	0.0960 (1)	x	x	174 (3)	B ₁₁	B ₁₁	94 (3)	B ₁₂	B ₁₂	44.2 (1)
Ag(2')	64(g)	0.0843 (14)	x	x	619 (41)	B ₁₁	B ₁₁	550 (4)	B ₁₂	B ₁₂	9.1 (1)
Ag(3)	96(i)	0.0	0.2205 (12)	0.2114 (10)	423 (39)	523 (81)	225 (42)	0.0	0.0	-109 (33)	7.3 (2)
Al(U)	8(b)	0.0	0.0	0.0	2.0 ^c						0.9 (1)

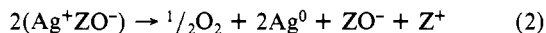
^a Anisotropic displacement parameters are given as $10^5 \exp[-\sum_{i,j} \Sigma_{k,l} B_{ijkl} h_i h_j k_l]$. ^b Values in parentheses represent the estimated standard deviations (esd) in terms of the least units cited for the values to their immediate left. ^c Isotropic displacement parameter B (in Å²).

treatment of Ag-exchanged zeolite A with a dilute aqueous solution of NH₃ removes 44% of the silver ions as Ag(NH₃)₂⁺ is excluded from the zeolite:



Simple hydrolysis can also occur during ion exchange.

Ag-exchanged zeolites lose oxygen when heated, and silver ions are reduced, according to the formal reaction



where ZO⁻ is the zeolite framework. White samples of Ag-exchanged zeolite A turn yellow and ultimately become brick red.^{4,5} Evidence for neutral or nearly neutral Ag atoms is provided by interatomic distances from X-ray diffraction data. For zeolite A, the electron density concentrations were assigned either to octahedral metal clusters enclosed in a cube of eight Ag⁺ ions at the centers of 6-rings of a sodalite unit⁶⁻¹¹ or to near-linear triplets Ag₃^{x+} with unknown charge x composed of two terminal silver species (probably near Ag⁺) at the center of adjacent 6-rings and a central silver species (probably near Ag⁰) in front of a 4-ring.^{12,13} Because the electron density is averaged over all sodalite units of a single crystal, there is no simple crystallographic distinction between an octahedron of six Ag⁰ in only one out of six sodalite units and a central Ag species of a triplet in all six sodalite units. However, triplets rather than octahedral clusters were interpreted to give a better explanation of H₂ and O₂ chemisorption⁵ and of color formation at low dehydration temperature and silver loading. Yellow samples have noninteracting Ag₃^{x+} triplets whereas brick red ones have pairs of interacting triplets that effectively combine into an Ag₆^{y+} hexuplet. Reflectance spectroscopy¹³ also favors small clusters over large metal particles.

The present structure determination was made on a crystal of Ag-exchanged zeolite A that had lost some Ag upon treatment with NH₄OH solution (ion exclusion effect) and that had undergone autoreduction of Ag upon dehydration.

Specimen Preparation

Crystals of zeolite 4A were prepared by a modification of Charnell's method¹⁴ including a second crystallization using seed crystals from the

first synthesis. Some crystals were then placed in a small volume of 0.025 M AgNO₃ solution for 90 min. Electron microprobe analysis demonstrated complete exchange. Longer contact with the silver nitrate solution destroyed the crystals. The silver-exchanged crystals were washed in distilled water and immersed in dilute ammonium hydroxide solution for 65 h. Both exchanges were performed in the dark to prevent photochemical reduction of silver. The crystals were still intact and transparent but had become brown-yellow. After washing, a cube, 0.079 mm on edge, was lodged in a quartz capillary and dehydrated for 2 days under 10⁻⁵ torr. The temperature was raised to 410 °C (683 K) over 270 min and kept constant for 41 h. The crystal was sealed at this temperature and slowly cooled to room temperature. It was dark red and crystalline, as checked by oscillation and Weissenberg photographs.

Electron microprobe analysis was made on a crystal of the same batch. It was mounted in epoxy and polished with 0.25-μm diamond paste before being coated with a carbon film. Calibration factors of the different elements were determined from An70 glass for Ca, Si, Na, and Al, Asbestos microcline for K, and silver metal for Ag. The wavelength analyses were corrected by the MAGIC program.¹⁵ Because of lack of standards containing both Ag and O, the analysis for Ag may be somewhat inaccurate: it should be correct to ~5% of the amount present, but a firm value cannot be given. Furthermore, the analyses for Al and Si should be more inaccurate than those for the original as-synthesized Na variety and the Ca-exchanged form.¹⁶ Taken strictly at face value, the electron microprobe analysis indicates the following unit-cell content before dehydration when calculated to 384 oxygen with H added to balance the charges: H₂₆Ag₇₀Si₉₆Al₉₆O₃₈₄·xH₂O. If the Si/Al ratio is greater than unity, as indicated by both electron microprobe analyses and X-ray diffraction data (e.g., refs 16 and 17), some adjustment is needed. For Si/Al = 1.05, the unit cell would contain 24 H, 98 Si, and 94 Al atoms. A 5% error in Ag would change H by 3.5. There is a minor problem because of evidence that 0.9 atom of Al was removed from the framework (see later). X-ray refinement (see later) indicated 66 Ag atoms per cell. When all the evidence is considered simultaneously, the unheated crystal has approximately 26 H and 68 Ag atoms, which corresponds to removal of ~28% of the silver atoms by complexing with NH₃. It will be assumed that the electron microprobe analysis applies to the volume of crystalline material.

X-ray Data Collection

An octant of data out to $(\sin \theta)/\lambda = 0.59$ was collected with monochromatized Cu Kα radiation on a Picker FACS-1 diffractometer using the θ - 2θ scan technique. Each reflection was scanned at a constant rate of 1.0° min⁻¹ and a range of 1.0-1.6°. Background intensity was counted at each end of a scan range for a fixed time of 40 s. After absorption correction (absorption coefficient 215 cm⁻¹), 3397 symmetry-related diffractions were averaged, yielding 693 unique diffractions of which 419 unique diffractions were above background at the 2σ level. Lorentz and polarization factors were applied and errors calculated as in ref 17. A total of 347 diffractions belong to the average structure in $Pm\bar{3}m$ ($a = 12.27$ Å) and 69 to the superstructure ($a = 24.54$ Å). All superstructure diffractions obey $Fm\bar{3}c$ ¹⁸ at the 2σ level except for 111 with intensity 400 ± 64, 23,7 with 39 ± 16, and 11,11,11 with 38 ± 31. There was no evidence for noncubic geometry, as was reported in ref 19 for a 4A

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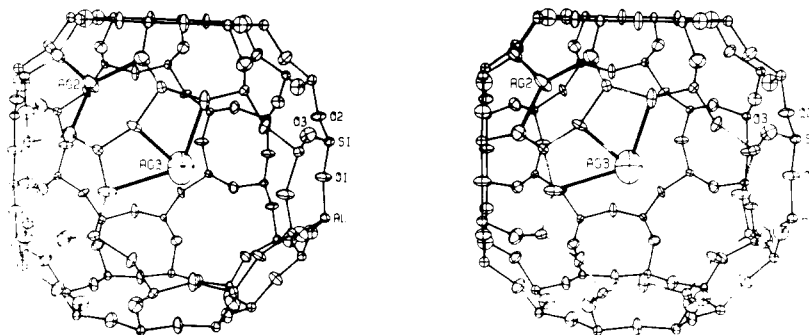


Figure 1. Stereoplots of the large cage of silver hydrogen zeolite A with silver sites Ag(2) and Ag(3). Only one position is shown for each site. Displacement ellipsoids are at the 50% probability level.

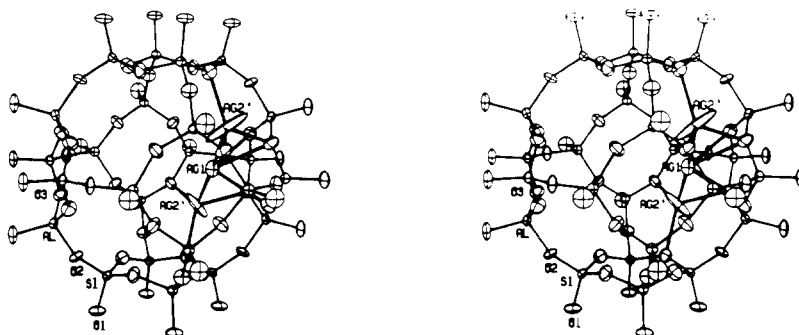


Figure 2. Stereoplots of the sodalite cage of silver hydrogen zeolite A with silver sites Ag(1) and Ag(2'). One Ag(1) and two Ag(2') sites are joined to represent a linear triplet, but it must be emphasized that the X-ray evidence is equivocal. Displacement ellipsoids are at the 50% probability level.

specimen. The cell dimension ($24.548 \pm 3 \text{ \AA}$) was obtained by a least-squares refinement with use of 2θ angles for 15 Friedel pairs ($44^\circ < 2\theta < 70^\circ$) and weighted wavelength 1.5418 \AA for Cu K α .

Structure Refinement

Refinement was successful with space group $Fm\bar{3}c$, as in ref 2, 16–18 and 20, with use of conventional least-squares²¹ and difference-Fourier techniques.²² Interatomic distances and angles were calculated with the program ORFFE,²³ and drawings were made with the plotting program ORTEP.²⁴ Atomic scattering factors, corrected for anomalous scattering corrections for Si^{2+} , Al^+ , O^- , and Ag^+ , were taken from ref 25. Factors for Si^{2+} and Al^+ were interpolated between factors for Si and Si^{3+} and for Al and Al^{3+} .

Refinement of the framework atoms and Ag(1) and Ag(2) converged rapidly to conventional agreement factors R and R_w of 0.070 and 0.104, respectively, for intensities uncorrected for absorption. A difference-Fourier peak displaced from the center of the 8-ring was modeled by Ag(3) in a special position off the diagonal (Table I, $y \neq z$), and refinement yielded 0.057 and 0.064 for R and R_w . Because Ag(2) did not account for all the electron density near the center of the 6-ring, Ag(2') was added to account for a difference-Fourier peak of height $6 e/\text{\AA}^3$. Refinement of Ag(2') lowered R and R_w to 0.038 and 0.043, but the anisotropic displacement factors (Table I) are rather large. Because Ag(2) and Ag(2') are only 0.5 \AA apart, there is considerable interaction in the least-squares matrix, and the strong elongation of the ellipsoids (i.e., high β_{12} , Table I) may be masking a range of atomic positions rather than just two positions. An absorption correction reduced R and R_w to 0.035 and 0.038.

At this stage, the only significant peak in the difference-Fourier map was at the origin in the center of the sodalite unit. Its height ($4.6 e/\text{\AA}^3$)

Table II. Selected Interatomic Distances (\AA) and Angles (deg) for $\text{Ag}_{1-2n}\text{H}_n\text{A}$

Si-O(1)	1.579 (12)	Al-O(1)	1.711 (12)
Si-O(2)	1.582 (12)	Al-O(2)	1.728 (12)
2 Si-O(3)	1.615 (8)	2 Al-O(3)	1.738 (8)
mean	1.598	mean	1.729
Si-O(1)-Al	150.1 (4)	Si-O(3)-Al	143.5 (2)
Si-O(2)-Al	157.7 (3)		
O(1)-Si-O(2)	109.2 (3)	O(1)-Al-O(2)	108.6 (5)
2 O(1)-Si-O(3)	111.3 (2)	2 O(1)-Al-O(3)	112.2 (2)
2 O(2)-Si-O(3)	108.5 (2)	2 O(2)-Al-O(3)	107.2 (2)
O(3)-Si-O(3)	108.0 (3)	O(3)-Al-O(3)	109.1 (3)
Ag(1)-4 O(3)	2.818 (6)	Ag(2)-3 O(3)	2.275 (3)
-4 Ag(2')	2.92 (3)	-3 Ag(1)	3.34 (1)
-4 Ag(1)	2.949 (9)	-Ag(2')	0.50 (2)
-3 Ag(2)	3.34 (1)		
Ag(2')-3 O(3)	2.30 (5)	Ag(3)-O(2)	2.37 (2)
		-O(1)	2.86 (3)
		-O(1)	2.64 (2)
Al(U)-6 Ag(1)	2.085 (6)	Al(U)-8 Ag(2)	4.081 (1)
-8 Ag(2')	3.58 (2)	-24 O(3)	4.568 (4)

falls in the range of $1-8 e/\text{\AA}^3$ found in the structure determinations of dehydrated A crystals exchanged with divalent cations (data collected in ref 26), and is attributed to an Al atom in a tetrahedral complex. Because decomposition of NH_4 -exchanged zeolites can lead to dealumination of the framework (ref 1, p 507), the origin peak in the present structure was modeled by Al(U). Least-squares refinement was successful only with fixed isotropic B , and $0.9 (1) \text{ \AA}$ Al was obtained for $B = 2$. Whereas a definite peak was found for an oxygen species at $x = y = z = 0.04$ in dehydrated Sr-A,²⁶ no evidence was found in the present structure because of the presence of Ag(1) inside the sodalite unit and because there might be 26 H atoms condensed with framework oxygens to form hydroxyl. It is not unlikely that occluded AlO_4 -bearing species would be spatially disordered over the unit in the present structure such that the electron density for oxygen would be lost in the background. A technical problem arises from absence of the inferred H atoms from the least-squares refinement. Probably they are implicitly accounted for by

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Table III. Comparison of Site Occupancies and Coordinates^a

specimen	no. of atoms in sites				
	4S	4L	6S	6L	8
dK-A ¹⁷	0.15 (x, 0.176)	0.5	1.5 (x, 0.162)	6.3 (x, 0.230)	3.0
dNa-A ¹⁶		0.8	7.8 (x, 0.199; B ₁₂ , 21)		2.8
dAg-A (oxidized) ¹⁰	0.5 (x, 0.173)		8.0 (x, 0.194; B ₁₂ , 91)		3.0
dAg-A (375 °C) ¹³	1.8 (x, 0.178)		3.5 (x, 0.172)	3.4 (x, 0.207)	2.1
dAg-A (430 °C) ¹³	1.1 (x, 0.19)		2.6 (x, 0.173)	4.7 (x, 0.201)	1.8
dAg-A (400 °C) ^{6,7}	2.1 (x, 0.171)		7.3 (x, 0.191; B ₁₂ , 136)		1.6
dAg-A (425 °C) ^{6,7}	3.6 (x, 0.168)		8.0 (x, 0.191; B, 148 Å ³)		0.9
dAg-A (450 °C) ⁷	3.5 (x, 0.168)		7.8 (x, 0.189; B ₁₂ , 130)		
C ₂ H ₂ -dAg-A ¹¹	2.6 (x, 0.165)		2.6 ^b (x, 0.188)	4.0 (x, 0.240)	1.7
dHAg-A (this paper)	0.7 (x, 0.170)		1.1 (x, 0.169)	5.5 (x, 0.192)	0.9
dNH ₄ -A ²		0.5	3.2 (x, 0.106)	5.4 (x, 0.258)	2.7
dAgTl-A ⁸	0.6 (Ag) (x, 0.151)		3.8 (Ag) ^c (x, 0.188)	2.4 (Tl) (x, 0.260)	3.0 (Tl)

^a Based on the pseudocell. Abbreviations: 4, opposite 4-ring; 6, near center of 6-ring; 8, near center of 8-ring; S, displaced into sodalite unit; L, displaced into large cage. Atomic coordinates and displacement factors ($\times 10^4$) are given for some positions. ^b Also 0.6 Ag(1) at 0.134, 0.134, 0.134. ^c Also 2.0 Ag(2) at 0.129, 0.129, 0.129.

the displacement factors of the oxygen atoms of the framework, but there might be a tendency to yield a positive peak at the origin. Further speculation is unprofitable, but it appears that any decomposition of the framework is small.

The final agreement factors are 0.034 and 0.033. The largest residual peaks in the final difference-Fourier map are at special positions (1.8 e/Å³ at 1/4, 1/4, 1/4; 1.1 e/Å³ at 0, 1/4, 1/4), and all other peaks are lower than 0.9 e/Å³.

Final atomic coordinates, and occupancy and displacement factors, are given in Table I, selected angles and distances in Table II, and drawings in Figures 1 and 2.

Results and Discussion

Framework. The overall mean T-O distances of 1.598 and 1.729 Å are similar to those of 1.597 and 1.731 Å for d-Na-A,¹⁷ 1.602 and 1.736 Å for d-KA,¹⁶ and 1.599 and 1.730 Å for d-SrA.²⁶ This confirms the earlier conclusion that Si and Al atoms essentially alternate on the tetrahedral nodes of zeolite A and rules out the model of ref 19. All of the data for zeolite A can be explained by geometrical flexing of the framework in response to change in physical conditions, disorder of the extraframework atoms from cell to cell, and chemical shifts in NMR patterns resulting from framework connectivity.²⁷ The present T-O distances are indicative of essentially complete occupancy of Si in the first tetrahedron and somewhat less than full occupancy (~90%) of the second tetrahedron by Al.²⁶

That the framework geometry of the present structure is fairly close to that of dNa-A,¹⁷ with maximum deviations of 8° in T-O-T and 3° in O-T-O angles, is not surprising. The occupancy of cation sites is fairly similar (Table III), and the smaller range of T-O-T angles (14°) in dAgH-A than in dNa-A (22°) and of O-T-O angles (4.2 vs. 6.3°) can be crudely attributed to decrease in "stress" from the 66 Ag compared to the 92 Na atoms.

The sequence of increasing distances from Al and Si to O(1), O(2), and O(3) in Table II can be simply explained by compensation for the extra bonding of Ag atoms to O(3) than to O(2) and O(1). It is interesting to speculate whether the postulated 26 H atoms are condensed with just one type of framework oxygen. Because a T-OH distance is expected to be about 0.05 Å longer than a T-O distance, the T-O(1) distances should be increased by (26/96)0.05 Å = 0.014 Å if all the H atoms were attached to O(1). This perturbation is too small for a confident conclusion to be drawn, but it can be stated that the general pattern of T-O-T and O-T-O angles does not indicate preferred attachment of H to one particular type of framework oxygen.

Silver Positions. The sum of 66.3 ± 0.5 atoms from the X-ray refinement is consistent with the estimate of 70 (±4?) from the electron microprobe analysis, especially as the error for the X-ray refinement does not take systematic error into account. Four sites are occupied fractionally by the Ag atoms, and it is important to recognize that a measured cation-oxygen distance is the average over all unit cells and that the real distance is likely to be somewhat

lower than the apparent distance because unbonded oxygens are likely to be further from a cation position than bonded oxygens.

Two-thirds (44) of the Ag atoms lie in site 2 nearly at the center of the 6-ring and are displaced into the large cage by only 0.12 Å from the plane of three O(3). As for bonding to all small cations in a 6-ring of zeolite A, three O(3) are pulled inward and three O(2) displaced outward, and the apparent distance of 2.27 Å from Ag(2) to O(2) is consistent with 3-coordination when compared to reference values for Ag⁺ of 2.17 and 2.52 Å for 2- and 4-coordination.²⁸

One-seventh (9) of the Ag atoms lie in site 2' displaced 0.38 Å from the center of the 6-ring into the sodalite unit, and the apparent distance of 2.30 Å is also consistent with 3-coordination. As discussed under Structure Refinement, it is not certain whether there are two clearly distinct sites 2 and 2', and Kim et al. preferred to use elongated displacement ellipsoids⁶⁻¹¹ whereas Gellens et al. used split sites^{12,13} (Table III).

Seven Ag atoms occupy site 3 displaced from the center of an 8-ring at apparent distances of 2.37 Å to O(2) and 2.64 and 2.84 Å to two O(1). Undoubtedly this type of Ag atom has a one-sided coordination as for dNa-A¹⁷ and dK-A,¹⁶ but the low occupancy (7 Ag in 96 positions) means that the apparent distances are determined almost entirely by unbonded oxygens. Perhaps the elongation of the displacement ellipsoids of O(1) and O(2) in Figure 1 is composed in part of displacements caused by bonding to Ag(3).

The most interesting Ag site is type 1 in front of a 4-ring in the sodalite unit (Figure 2). The 6 Ag atoms occupy a 48-fold position and the apparent distance to four O(3) is 2.82 Å. Furthermore, each Ag(1) site is at 2.95 Å to four other Ag(1) sites and 2.92 Å to four Ag(2') sites. From the purely crystallographic viewpoint, all proposals about the related occupancy of Ag(1) and Ag(2') sites are speculative, but the physicochemical properties described in the Introduction are consistent with formation of some kind of metal cluster.

For assistance in the discussion of the crystallographic evidence on the metal cluster, Table III summarizes the cation positions for selected structures with use of the pseudocell for convenience. Because so many numbering schemes have been used, the sites are labeled with obvious acronyms: 4, opposite the 4-ring; 6, near the center of the 6-ring on a body diagonal; 8, near the center of the 8-ring; S, displaced into the sodalite unit; L, displaced into the large cage. There is a strong tendency for the eight 6-ring sites to be filled when univalent cations are present in sufficient numbers, but even for dNa-A and dK-A there appears to be a small deficiency (0.2 atom). The present structure for dHAg-A has a total of only 6.6 Ag near the 6-rings, even though 1.6 atoms reside elsewhere. Whereas the 0.7 Ag atom in 4S can be attributed to a metal cluster that forbids entrance into a 6-ring, it is not obvious why 0.9 Ag enter an 8-ring where the one-sided coordination

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dination is inferior to the near-planar coordination at a 6-ring. Perhaps some of the unlocated H atoms are effectively occupying 6-rings as a result of condensation with framework oxygens. To fill the 6-rings with univalent species, 1.4 H per pseudocell are needed; this corresponds to only 11 out of the postulated 26 H per supercell.

The consistent occupancy of site 4S by Ag in the Ag-bearing structures is demonstrated clearly in Table III, and there can be no doubt about an unusual bonding character, as recognized by Kim and Seff.⁶ In particular, for dHAg-A (Figure 2), Ag(1) in a 4S site lies at 2.82 Å to four O(3) and at 2.92 Å to four Ag(2') sites of type 6S and 2.95 Å to four other Ag(1) sites. In principle, the occupancies of Ag(1) and Ag(2') sites are sufficiently small for dHAg-A that there need not be a close approach between them. Even an increase of the occupancy of Ag(1) from 0.7 to 1.0 would still allow four Ag(2') sites to be occupied without a close approach. However, this interpretation does not explain why Ag(1) is at 2.82 Å from four O(3) when the bonding distance for 4-coordination should be shorter; cf. 2.52 Å for square-planar coordination²⁸ of Ag⁺ and 2.59–2.61 Å for one-sided four-coordination of Na(3) in dNa-A.¹⁸ Furthermore, (a) the physico-chemical history of dHAg-A should have produced some reduced Ag atoms, (b) extended-Hückel molecular orbital calculations indicate that an Ag–Ag bond in a cluster is strong and interaction with a framework oxygen is weak,²⁹ and (c) the red color of dHAg-A is in favor of cluster formation.^{5–13,29,30}

An important question is the size and shape of the cluster. In principle, some information on the size and shape of the cluster might be inferred from the relative populations of sites 4S and 6S;¹³ a linear triplet Ag⁺(6S)–Ag⁰(4S)–Ag⁺(6S) requires twice as many atoms in 6S as in 4S, whereas an octahedral cluster of six Ag⁰(4S) inside a cube of eight Ag⁺(6S) requires a ratio of 1.33 for Ag(6S)/Ag(4S). In practice, the crystallographic evidence is equivocal because of the overlapping of electron density along the body diagonal through the center of the 6-ring. Whereas Kim and Seff^{6–11} successfully refined their structures with a single ellipsoid centered on $x = y = z \approx 0.19$ and strongly elongated along the body diagonal with root-mean-square displacement 0.46–0.58 Å, Gellens et al.¹³ used two ellipsoids whose centers are displaced 0.6–0.7 Å apart and whose weighted mean position is near $x = y = z \approx 0.19$. The two refinements by Gellens et al. in Table III were obtained from X-ray powder data for which redundancy of $h^2 + k^2 + l^2$ causes reduced accuracy over single-crystal data. The refinements of Ag(2) and Ag(2') in the present structure determination are unsatisfactory because of overlap of the displacement ellipsoids; thus the rms displacements of 0.17 and 0.48 Å for Ag(2) and Ag(2') are comparable to the distance of 0.50 Å between the centers of the ellipsoids. If it is taken at face value, the population ratio of 9.1 (1)/5.7 (1) = 1.60 (5) for Ag(2') and Ag(1) is intermediate between the theoretical extremes of 2 and 1.33 for a linear triplet and an octahedron. However, it seems best to regard the present evidence as inconclusive, especially as the role of the missing H atoms is unknown. In order to reduce the problem of poor resolution between atoms in 6S and 6L sites, it is desirable to decrease the thermal displacements by collecting diffraction intensities at low temperature. Appropriate structure determinations by Kim and Seff will be repeated at liquid nitrogen temperature to test whether the size of metal clusters can be determined from electron-density peaks.

Whatever the size of the metal cluster in the dehydrated Ag-exchanged varieties of zeolite A, it is quite certain that the Ag species in the 4S site cannot be considered to be chemically and

physically identical with Ag atoms in metallic silver. Even for the octahedral cluster postulated by Kim and Seff,^{6,7} each Ag atom in a 4S site is linked to four Ag atoms, each bonded to three oxygens, and is only 2.8 Å from four O(3) atoms. The four Ag atoms must have a strongly ionic character, and the interaction between Ag in 4S and the four O(3) atoms cannot be ignored since the Ag–O(3) distance is only 0.2 Å longer than the Na(3)–O distances in dNa-A.¹⁷

Finally, it is interesting to speculate whether there might be any interaction between Na atoms in 4- and 6-ring sites of dNa-A¹⁷ and for K atoms in dK-A.¹⁶ In the former, the 4-ring sites project into the large cage and are far apart. The distance of 3.70 Å between Na(3) in a 4L site and Na(1) in a 6-ring is less than twice the atomic radius of 1.91 Å,²⁸ and some weak interaction might occur even though both Na(1) and Na(3) appear to be bonded ionically to framework oxygens. The situation is more complex for dK-A because all four types of 4S, 4L, 6S, and 6L sites are occupied (Table III). It was assumed in ref 16 that sites 4S and 6S were not occupied simultaneously, and similarly this was also assumed for 4L and 6L. There is no obvious explanation why the 4S site is occupied by K when it is not occupied by Na. The atomic radius of K is large (1.38 Å),²⁸ and the 4S site is only 2.8 Å from the 6S site and 4.1 Å from the 6L site. Furthermore, the distance from the 4S site to the four O(3) atoms is rather long at 2.99 Å. The possibility of a weak interaction of metallic nature should be considered and experiments made at low temperature to test whether the bonding character changes.

Aluminum–Oxygen Complex. Although the crystallographic evidence for an aluminum–oxygen complex is not convincing (see earlier), the observations of dealumination of NH₄ zeolites during decomposition^{1,31–33} make it plausible that the electron density peak at the cell origin represents Al and that oxygen is present to generate some kind of aluminum–oxygen complex.³⁴ The amount of such a complex is too small to affect the Ag in the 4S site.

Hydrogen. There is no direct crystallographic evidence concerning the position of the inferred H atoms, and no indication that the positions of the Ag species are related to those of the H atoms, except for the possible influence (see earlier) that the H atoms have condensed with more than one type of oxygen atom. Unfortunately, the present crystal is too small for single-crystal neutron diffraction, and powder techniques are not likely to have enough discrimination to detect the H atoms. If the 5.7 Ag atoms have effectively zero charge, and the aluminosilicate framework is intact, it may be necessary to adjust the number of inferred H atoms from 26 (see Specimen Preparation) to 32.

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

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