Communications to the Editor

Structure of a Very Small Piece of Silver Metal. The Octahedral Ag_6 Molecule. Two Crystal Structures of Partially Decomposed Vacuum-Dehydrated Fully Ag^+-Exchanged Zeolite A

Sir:

It was reported that polynuclear cations of mean or approximate composition $Ag_3{}^+$ form upon partial reduction of dehydrated fully Ag^+-exchanged zeolite Y.[1] It now appears probable that uncharged silver clusters, the molecules Ag_6, have formed within cubes of eight Ag^+ ions in fully Ag^+-exchanged zeolite A dehydrated under vacuum at elevated temperatures.[2]

The structures of small metal clusters are of interest because of the pronounced catalytic activity of some highly dispersed metals, notably platinum, palladium, and nickel. These three are isostructural with silver.

Crystals of sodium zeolite 4A (stoichiometry: $Na_{12}Si_{12}Al_{12}O_{48}{\cdot}27H_2O$) were prepared by Charnell's method,[3] modified by the inclusion of seed crystals. Complete Ag^+-exchange of two zeolite A single crystals ~0.085 mm on an edge was achieved by allowing 0.05 N aqueous $AgNO_3$ to flow past each crystal at the rate of ~1 cm/s for 5 days. Dehydration occurred at 400 °C for 4 days (2 days at 10^{-5} Torr and 2 days in 100 Torr O_2) for one crystal, and 10^{-5} Torr and 425 °C for 10 days for the second. In each case, the clear, colorless, hydrated, exchanged crystal initially became black. This color lightened to brick red and ultimately to a clear golden yellow during the first few days of the dehydration treatment. (A similarly exchanged and treated bulk sample was bright dark gold in color.)

The space group *Pm*3*m* (no systematic absences) was used throughout this work for reasons discussed previously.[4] All 888 unique reflections for each crystal for which $2\theta < 70°$ were examined by counter methods on a fully automated Syntex $P\bar{1}$ diffractometer with monochromatic Mo Kα radiation (λ_1 = 0.70930 Å, λ_2 = 0.71359 Å) and a pulse-height analyzer. Relatively large data sets, 416 and 441 unique reflections, respectively, were used for structure solution and refinement. Other experimental details, including data reduction, are the same as previously described.[4] The resulting structures were refined by full-matrix least-squares methods to final weighted R_2 indices, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$, of 0.110 and 0.076, respectively. In both structures, a = 12.295 (2) Å and eight Ag^+ ions at Ag(1) are located at 6-ring sites, filling them all. In the first structure (Tables Ia and II), 2.0 Ag^+ at Ag(3) are found in 8-ring sites, and 2.0 are in the sodalite unit at Ag(2) where they represent neutral Ag atoms. Upon further dehydration (the second structure, Tables Ib and II), the latter two numbers become 0.5 and 3.5, respectively.

It is proposed, consistent with previous reports,[5,6] that oxide ions of the zeolite framework have been oxidized to O_2, and that Ag^+ ions have been correspondingly reduced. It is proposed that the eight 6-ring Ag^+ ions per unit cell, those of the twelve whose coordination environment is the most adequate, are relatively stable with respect to reduction under the conditions employed, consistent with previous results on silver-exchanged zeolite X.[7] The less suitably coordinated Ag^+ ions, such as the 8-ring Ag^+ ions, and any zero-[8,9] or near-zero-coordinate[10] Ag^+ ion that might have formed upon dehydration, are progressively reduced. The second crystal studied would then have progressed further (about seven-eighths of the way) toward the completion of the reaction, the reduction of four non-6-ring Ag^+ ions per unit cell. The general formula per unit cell is $Ag^+{}_{12-2x}Ag^0{}_{2x}Si_{12}Al_{12}O_{48-x}$; x = 1.0 and 1.75, respectively, in the two samples studied. No framework

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

Atom	Wyckoff position	x	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor	
											Fixed[c]	Varied
A. The Structure with 2.0 Ag Atoms per Unit Cell												
(Si, Al)	24 (*k*)	0	1839 (4)	3695 (4)	29 (4)	18 (4)	28 (4)	0	0	13 (6)	1[d]	1[d]
O(1)	12 (*h*)	0	2119 (17)	½	108 (28)	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	⅓	0.35 (1)
Ag(3)	12 (*i*)	0	4223 (24)	4223 (24)	394 (79)	321 (46)	321 (46)	0	0	−54 (102)	⅙	0.13 (1)
B. The Structure with 3.5 Ag Atoms per Unit Cell												
(Si, Al)	24 (*k*)	0	1824 (3)	3691 (3)	16 (2)	11 (3)	13 (2)	0	0	6 (4)	1[d]	1[d]
O(1)	12 (*h*)	0	2080 (12)	½	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	7/12	0.60 (1)
Ag (3)	24 (*m*)	242 (16)	4356 (29)	4359 (29)	78 (213)	81 (36)	81 (36)	−17 (67)	−67 (67)	−15 (82)	1/48	0.036 (3)

[a] Positional and anisotropic parameters are given ×10^4. Numbers in parentheses are the estimated standard deviation 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] Root mean square displacements can be calculated from β_{ii} values using the formula, $\mu_i = 0.225\, a(\beta_{ii})^{1/2}$, where a is the cell constant, 12.295 Å. [c] All crystallographic parameters and esd's, with the exception of those in the next (last) column, were calculated using these internally consistent occupancies. [d] Occupancy for (Si) = ½; occupancy for (Al) = ½.

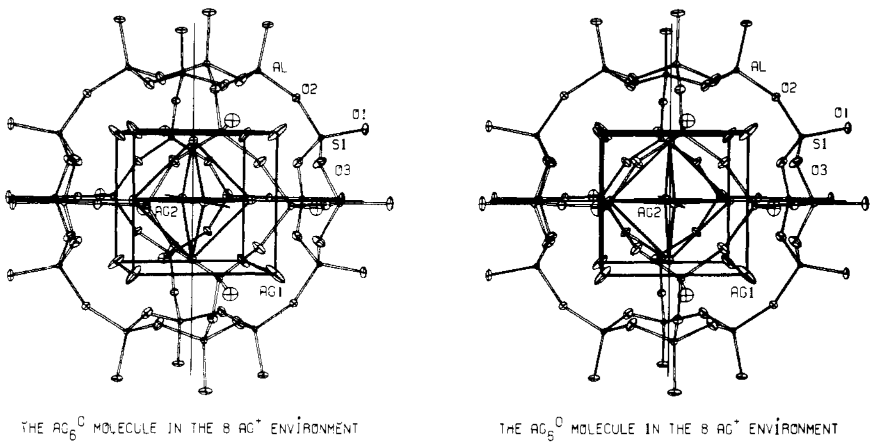

Figure 1. A stereoview of a sodalite unit containing an octahedral Ag_6 molecule within a cube of eight Ag^+ ions is shown using ellipsoids of 20% probability. The ions at Ag(3) occupy 8-ring sites and are not shown.

oxide vacancies could be found.

The largest cluster in the latter structure must be six, five, or four silver atoms in size. It must have the form of an octahedron with zero, one, or any two atoms missing, respectively. However, the tendency of Pd and Pt atoms produced at low densities in zeolite Y to agglomerate into small clusters,[11,12] instead of retaining a constant occupancy in each unit cell or sodalite unit, has been established, and is presumed to occur in this structure also. It is difficult to believe that a four-atom cluster (in the form of a square or alternatives of lower symmetry) or a five-atom cluster (an octahedron with one vertex missing) is more stable than the highly symmetric six-atom cluster whose structure resembles that of silver metal so closely. All possible clusters smaller than six atoms in size would be required by these results to have a lower symmetry than their environment. The discussion which follows assumes, based upon these incomplete arguments, that only six-atom clusters exist, and shows that the resulting structure is reasonable.

All of the sodalite units in the crystal contain eight Ag^+ cations, each nearly at the center of one of the eight 6-rings per sodalite unit (see Figure 1). Each Ag^+ ion (B = 5.9 $Å^2$) approaches three oxide ions of the zeolite framework at a distance of 2.25 Å; this interaction is responsible[13] for the yellow color of the crystal. On the surface of each sodalite unit, and consistent with its high symmetry, O_h, these eight Ag^+ ions at Ag(1) lie at the corners of a cube, 4.69 Å on an edge (see Figure 1).

The following discussion assumes an idealized stoichiometry of $Ag^+{}_8Ag^0{}_4Si_{12}Al_{12}O_{46}$ per unit cell. One-third of the sodalite units are otherwise empty of silver species. The remaining two-thirds each contain a cluster of six silver atoms (B = 1.8 $Å^2$) at Ag(2) arranged in the form of a perfect octahedron at the center of the sodalite unit and in an orientation fully consistent with the symmetry of its environment. The Ag-Ag distance in the cluster is 2.93 Å, slightly more than the Ag-Ag distance in silver metal, 2.89 Å. The six-atom cluster is closest packed, and is like a piece 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 (see Figure 1).

The eight Ag^+ ions per unit cell lie on the threefold axes of the Ag_6 cluster. Each Ag^+ ion (at Ag(1)) is 3.33 Å from three Ag atoms. Except for this longer (than 2.93 Å) distance, all 14 Ag atoms and ions are arranged in a cubic closest-packed manner, precisely as in a classroom model of a face-centered cubic unit cell. Each Ag_6 cluster is stabilized within the zeolite by coordination to these eight Ag^+ ions.

Table II. Selected Interatomic Distances (Å) and Angles (Degrees)[a]

	2.0 Ag^0 structure[b]	3.5 Ag^0 structure[b]
(Si, Al)-O(1)	1.641 (7)	1.639 (4)
(Si, Al)-O(2)	1.642 (15)	1.658 (10)
(Si, Al)-O(3)	1.670 (11)	1.677 (7)
Ag(1)-O(3)	2.311 (13)	2.249 (9)
Ag(2)-O(3)	2.835 (15)	2.785 (8)
Ag(3)-O(2)	2.221 (33)	2.461 (42)
Ag(1)-Ag(2)	3.338 (3)	3.327 (2)
Ag(2)-Ag(2)	2.972 (8)	2.928 (4)
O(1)-(Si, Al)-O(2)	112.1 (9)	112.2 (6)
O(1)-(Si, Al)-O(3)	108.7 (9)	111.1 (6)
O(2)-(Si, Al)-O(3)	109.1 (7)	107.5 (5)
O(3)-(Si, Al)-O(3)	108.9 (10)	107.1 (5)
(Si, Al)-O(1)-(Si, Al)	155.8 (9)	157.9 (5)
(Si, Al)-O(2)-(Si, Al)	158.4 (10)	156.5 (7)
(Si, Al)-O(3)-(Si, Al)	146.6 (10)	142.1 (7)
O(3)-Ag(1)-O(3)	119.8 (7)	119.6 (4)
O(3)-Ag(2)-O(3)	57.3 (6)	58.0 (3)
Ag(1)-Ag(2)-Ag(1)	89.6 (2)	89.6 (1)

[a] These distances and angles, except for that involving Ag(3), can be found in Figure 1. [b] The structures are identified by the average number of reduced silver atoms per unit cell. Each is considered to contain neutral Ag_6 molecules in 33 or 58% of the unit cells (or sodalite units), respectively.

A third crystal structure indirectly provides additional support for the proposal that Ag^+ ions are reduced by framework oxide ions. A crystal of Ag_{12}-A, prepared like the other two, was dehydrated under more strenuous conditions, 10^{-5} Torr and 475 °C for 7 days. The resulting crystal 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 diffracted intensity from silver appeared to be comparable with that from the zeolite. The unit cell constant of this zeolite crystal had decreased sharply from 12.295 (2) Å to 11.42 (2) Å, however, and only a few very broad reflections (width at half-maximum ~1.5° in 2θ) could be observed. This indicates that the crystal has been damaged, consistent with an expected loss of up to six of the 48 framework oxide ions per unit cell. Altogether, it is clear that Ag^+ ions have been reduced by zeolite oxide ions. A crude least-squares experiment was performed on this third crystal in which only the scale factor and the occupancies of Ag(1) and Ag(2) were varied, using the very small data set observed, only eight reflections. The results indicated that two Ag^+ ions and two Ag atoms remained per unit cell. That is, 10 of the original 12 Ag^+ ions had been reduced. This suggests the conclusion, reached earlier from a consideration of the structure of an ethylene complex[14] of dehydrated Ag_{12}-A which contained ~3.0 Ag atoms per unit cell, that a minimum of six Ag^+ ions are needed to stabilize an Ag$_6$ cluster. The complex would therefore be (Ag$^+$)$_6$Ag$_6$. When fewer ions are available per cluster, silver atoms migrate to the zeolite surface.

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Supplementary Material Available: A listing of the observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

References and Notes

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Synthesis and Structures of Two New Hydrides of Nitrogen, Triazane (N_3H_5) and Cyclotriazane (N_3H_3). Crystallographic and Mass Spectrometric Analyses of Vacuum-Dehydrated Partially Decomposed Fully Ag$^+$-Exchanged Zeolite A Treated with Ammonia

Sir:

Ammonia gas at 1 atm and room temperature was sorbed onto a single crystal of vacuum-dehydrated partially decomposed fully Ag$^+$-exchanged zeolite A, Ag$_{12}$-A.[1] Subsequent crystallographic analysis indicated the presence of three molecules of triazane, N_3H_5, and four molecules of cyclotriazane, N_3H_3 (quite high concentrations), per unit cell. The formation of these new molecules was confirmed by a mass spectroscopic analysis of the vapor phase above the zeolite from 25 to 90 °C. Both N_3H_3 and N_3H_5, the first neutral saturated hydrides of nitrogen to contain more than two nitrogen atoms per molecule, are stabilized within the zeolite by complexation to Ag$^+$ ions and by hydrogen bonding to the zeolite framework. This reaction sequence was initially done to effect a mild reduction of Ag$^+$, to prepare metal atoms and stable clusters within the zeolite.

It is now understood that neutral clusters of silver atoms, probably Ag$_6$,[1] had already formed before ammonia was introduced. The zeolite lattice also contained Ag$^+$ ions and three-coordinate Al^{3+} and Si^{4+}; so several sites of possible catalytic importance are present. Apparently the triazanes are more nucleophilic than Ag$_6$, because the Ag$_6$ molecules have been displaced from their complexes with Ag$^+$ and have left the zeolite to form crystallites of silver metal on the surface. The silver atoms or small clusters diffusing out of the zeolite (Ag$_6$ is too large to diffuse intact) may also be catalytically active.

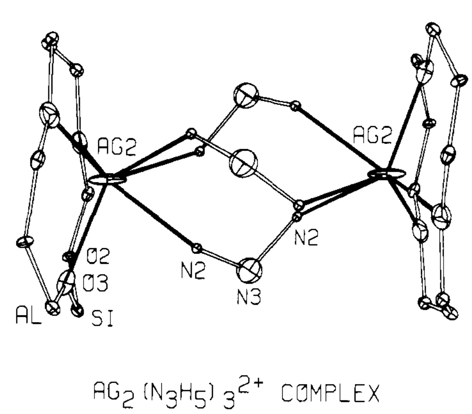

Figure 1. The $Ag_2(N_3H_5)_3^{2+}$ cation in the sodalite unit. Selected bond lengths are Ag(2)-O(3) = 2.39 (3), Ag(2)-N(2) = 2.45 (2), and N(2)-N(3) = 1.6 (1) Å. Some bond angles are O(3)-Ag(2)-O(3) = 107 (1), N(2)-Ag(2)-N(2) = 65 (1), Ag(2)-N(2)-N(3) = 134 (5), and N(2)-N(3)-N(2) = 107 (8)°.

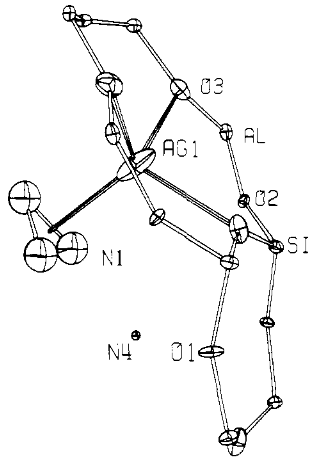

Figure 2. One of the four $Ag(N_3H_3)^+$ complexes in the large cavity of each unit cell. Selected bond lengths are Ag(1)-O(3) = 2.46 (2), Ag(1)-N(1) = 2.59 (5), N(1)-N(1) = 1.49 (8), N(1)-N(4) = 2.53 (12), and N(4)-O(1) = 2.86 (5) Å.

Crystals of sodium zeolite 4A (stoichiometry: $Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$) were prepared by Charnell's method,[2] modified by the inclusion of seed crystals. A single crystal 0.08 mm on an edge was selected and lodged in a fine glass capillary. $AgNO_3$ (0.05 F) was allowed to flow past the crystal at ~1.5 cm/s for 5 days, after which the crystal was dehydrated for 60 h at 400 °C and 1×10^{-5} Torr. Then the crystal was treated at 400 °C with 100 Torr of zeolitically dried oxygen for 3 days. After it was returned to ambient temperature (23 °C), the oxygen gas was evacuated. Microscopic examination indicated that the crystal was not damaged, but that its color had changed from colorless to golden yellow. At this point, the crystal was treated with a continuous stream of zeolitically dry ammonia gas at 765 Torr and 23 °C for 36 h, and became black. After evacuation for a few minutes at 23 °C, the capillary containing the crystal was removed from the vacuum line by torch.

The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[3] All 597 unique reflections for which $3° < 2\theta < 60°$ were examined by counter methods on a fully automated Syntex $P\bar{1}$ diffractometer with monochromatic Mo Kα radiation and a pulse-height analyzer. Of these, only the 169 for which $I > 3\sigma(I)$ were used for structure solution and refinement. An absorption correction was judged to be negligible[4] and was not applied. Other experimental details including data reduction are the