are needed to stabilize an Ag_6 cluster. The complex would therefore be $(Ag^+)_6Ag_6$. When fewer ions are available per cluster, silver atoms migrate to the zeolite surface.

Acknowledgments. This work was supported by the National Science Foundation (Grant No. CHE76-81586). We are also indebted to the University of Hawaii Computing Center.

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

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Received February 14, 1977

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.

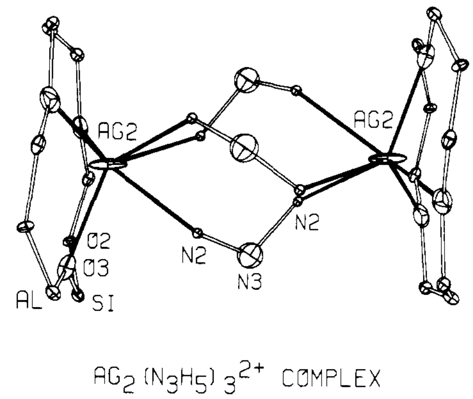

Figure 1. The $Ag_2(N_3H_5)_3{}^{2+}$ cation in the sodalite unit. Selected bond lengths are Ag(2)-O(3) = 2.39 (3), Ag(2)-N(2) = 2.45 (2), and N(2)-N(3) = 1.6 (1) Å. Some bond angles are O(3)-Ag(2)-O(3) = 107 (1), N(2)-Ag(2)-N(2) = 65 (1), Ag(2)-N(2)-N(3) = 134 (5), and N(2)-N(3)-N(2) = 107 (8)°.

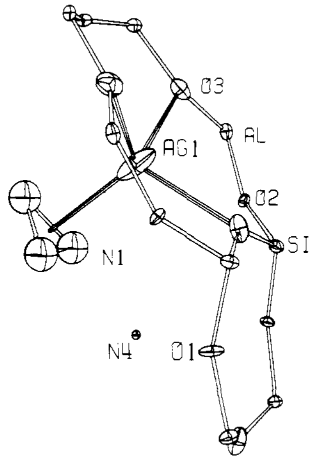

Figure 2. One of the four $Ag(N_3H_3)^+$ complexes in the large cavity of each unit cell. Selected bond lengths are Ag(1)-O(3) = 2.46 (2), Ag(1)-N(1) = 2.59 (5), N(1)-N(1) = 1.49 (8), N(1)-N(4) = 2.53 (12), and N(4)-O(1) = 2.86 (5) Å.

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

Table I. Positional, Thermal, and Occupancy Parameters for Vacuum-Dehydrated Partially Decomposed Fully Ag^+-Exchanged Zeolite A Treated with Ammonia[a]

Atom	Wyckoff position	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor Fixed[b]	Occupancy factor Varied[c]
(Si, Al)	24 (*k*)	0	1820 (9)	3703 (7)	29 (8)	46 (9)	18 (8)	0	0	−9 (15)	1[d]	1[d]
O(1)	12 (*h*)	0	2119 (25)	½	6 (24)	90 (42)	−6 (21)[e]	0	0	0	1	1
O(2)	12 (*i*)	0	3012 (16)	3012 (16)	9 (22)	32 (17)	32 (17)	0	0	92 (47)	1	1
O(3)	24 (*m*)	1097 (12)	1097 (12)	3320 (20)	60 (15)	60(15)	94 (25)	−27 (42)	−21 (32)	−21 (32)	1	1
Ag(1)	8 (*g*)	2343 (9)	2343 (9)	2343 (9)	136 (9)	136 (9)	136 (9)	174 (24)	174 (24)	174 (24)	½	0.47 (2)
Ag(2)	8 (*g*)	1416 (17)	1416 (17)	1416 (17)	85 (13)	85 (13)	85 (13)	137 (34)	137 (34)	137 (34)	¼	0.33 (3)
Ag(3)	12 (*i*)	0	4360 (24)	4360 (24)	378 (99)	232 (50)	232 (50)	0	0	−29 (108)	⅙	0.19 (1)
N(1)	24 (*m*)	2924 (57)	3786 (36)	3786 (36)	9 (3)						½	0.63 (8)
N(2)	6 (*e*)	0	0	1530 (42)	1 (1)						1	0.95 (16)
N(3)	12 (*i*)	0	1327(104)	1327 (104)	6 (7)						¼	0.33 (15)
N(4)	24 (*m*)	2330 (42)	2330 (42)	4870 (126)	−1.8 (2.0)[e,f]						⅙	0.18 (3)
N(5)	6 (*e*)	0	0	4907 (815)[g]	6 (7)						⅓	0.21 (7)

[a] Positional and anisotropic thermal parameters are given $\times 10^4$; isotropic thermal parameters are in $Å^2$. Numbers in parentheses are the estimated standard deviations in the least significant digits. See Figures 1 and 2 for the identities of the atoms. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] These rational occupancies are internally consistent. [c] As an addendum to least-squares refinement, the occupancy parameters of all of the silver and nitrogen atoms were included with all previously varied parameters in further least squares. At convergence, the values given in this column were observed. The freeing of the occupancies did not affect the error indices significantly. These parameters are included in the count of the total number of variables. All other values presented in this table and in this report are calculated using the fixed occupancies given in the adjacent column. [d] Occupancy for (Si) = ½; occupancy for (Al) = ½. [e] This physically unacceptable value was increased by 1σ in the preparation of Figure 2. [f] The correlation coefficient between the z and B parameters for this atom is high, 0.66. [g] The correlation coefficient between z and B for this atom is 0.78. On a Fourier function $z = 0.48$, with an esd judged to be <0.02, much less than that which emerged from least squares.

same as previously presented.[5] Full-matrix least-squares refinement using anisotropic thermal parameters for all atoms except N(3), N(4), and N(5), which were refined isotropically, converged to the error indices, $R_1 = (\Sigma|F_o - |F_c||/\Sigma F_o) = 0.127$ and $R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.094$. Removing the N_3H_3 molecules from least squares raises R_1 and R_2 to 0.161 and 0.133 at convergence, respectively. Removing only the N_3H_5 molecules raises the Rs to 0.186 and 0.158. Removing only the NH_3 molecules and NH_4^+ ions raises the Rs to 0.151 and 0.115. These are large increases which assure the presence of each major nitrogen species in the structure. Subsequent occupancy refinement of all silver and nitrogen positions led unambiguously to the values given in Table I. In total, 51 parameters were varied; of course, those 20 which describe the zeolite framework differ little from those in previous zeolite A structures, and may be omitted from the calculation of an overdetermination ratio, 169/31 = 5.5.

Three triazane molecules are complexed to two Ag^+ cations in the sodalite cavity (see Figure 1). The N-N single bond length, 1.6 (1) Å, can be compared with distances of 1.46 Å in N_2H_4 and $(CH_3)_2N_2H_2$,[6a] 1.75 Å in N_2O_4,[6b] and 1.43-1.47 Å in *N,N,N′,N′*-tetraaminopiperazinediium bis(azide)[6c]. The N-N-N angle in triazane (107 (8)°) agrees with the corresponding angle (108.7°) in *N,N,N′,N′*-tetraaminopiperazinediium bis(azide).[6c] The triazane molecules are stabilized in the zeolite by complexation to Ag^+ ions and by the hydrogen bonding of *all five* hydrogen atoms to O(3) ions of the zeolite framework: N(2)-O(3) = 2.89 (4) Å, N(3)-N(2)-O(3) = 125°, N(3)-O(3) = 2.8 (1) Å, and N(2)-N(3)-O(3) = 77°. The resulting $Ag_2(N_3H_5)_3^{2+}$ species has D_3 symmetry.

One of four equivalent cyclotriazane molecules complexed to Ag^+ in the large cavity is shown in Figure 2. The N-N bond length, 1.49 (8) Å, is about the same as the corresponding single-bond distances in the hydrazines.[6a] Cyclotriazane, because it has substantial π character, is able to form a lateral (axial) π complex with Ag^+. It is clear that this complex is weak because cyclotriazane is easily removed from the zeolite and because the N_3H_3 to Ag^+ interaction is long (Figure 2). Surprisingly, this complex has nearly the same geometry as one between cyclopropane and Co(II),[7] even though the metal ions have quite different electronic structures and the σ approaches made by the ligands are quite different: that of cyclopropane involves three hydrogen atoms, and cyclotriazane's presumably involves three lone pairs of electrons. Still, C_3H_6 is isoelectronic with cyclotriazane and has substantial π character for the same reasons. This C_3H_6 complex, in turn, is similar to various lateral complexes of alkenes and alkynes with transition metal ions,[3,8,9] including Ag^+.[10] Presumably the dative bond between the π system of N_3H_3 and Ag^+ has stabilized the ligand molecule. Further stabilization can arise from hydrogen bonding. Each N_3H_3 molecule hydrogen bonds (2.53 (12) Å) to an ammonia molecule at N(4), which in turn forms two hydrogen bonds to the zeolite framework: N(4)-O(1) = 2.86 (5) Å. The local symmetry of the N_3H_3 complex is found to be C_{3v}, within the accuracy of this determination.

The Ag(1)-O(3) and Ag(2)-O(3) bond lengths, 2.46 (2) and 2.39 (3) Å, respectively, are longer in this intrazeolitic complex than in dehydrated partially decomposed Ag_{12}-A, 2.31 (1) Å. The ions at Ag(1) and Ag(2) have moved substantially, 0.98 and 0.99 Å in opposite directions, along threefold axes to more tetrahedral positions upon complexation with the triazanes.

The Ag-N distances are Ag(2)-N(2) = 2.45 (2) Å, for the σ interaction (Figure 1), and Ag(1)-N(1) = 2.59 (5) Å, for the π interaction (Figure 2). These distances can be compared with Ag-N distances from 2.44 to 2.67 Å in $AgC(CN)_2NO_2$,[11] 2.21 Å in the silver nitrate pyrazine complex,[12] and 2.22 to 2.54 Å in bis[nitratobis(pentamethylenetetrazole)silver(I)].[13]

Further confirmation of the presence of the previously unknown molecules N_3H_3 and N_3H_5, and an indication of their stability in the gas phase, was obtained from mass spectra taken on the gases evolved from ~1 g of vacuum-dehydrated Ag_{12}-A which had been exposed to NH_3 at ~400 Torr for 40 h. At temperatures between ambient and 70 °C, peaks corresponding to $N_3H_3^+$ (*m/e* 45.0327 (calcd), 45.0336 (obsd)) and $N_3H_2^+$ (*m/e* 44.0249 (calcd), 44.0250 (obsd)), were observed and conclusively identified by their masses obtained at high resolution using a Varian MAT 311 instrument. As the temperature was raised further these two peaks remained virtually unchanged in intensity, but by 75 °C two new small peaks had appeared at *m/e* 46 and 47. While the intensities of these latter peaks were too low to permit high resolution data to be obtained, they have the nominal masses of $N_3H_5^+$ and $N_3H_4^+$. These results are entirely consistent with the structure of the zeolite complex—compared to triazane, cyclotriazane complexes Ag^+ at a longer distance and has easier access to the principal zeolite channels. Cyclotriazane would therefore be less tightly held within the zeolite and should be easier to remove than triazane.

The net reaction has not yet been determined. Hydrogen gas, an expected product, is not observed in sufficient quantity even upon heating. It appears that two Ag^+ ions have been reduced by one lattice O^{2-} to form the elements which migrated out of the zeolite during the dehydration step, and that two more Ag^+ ions have been reduced by NH_3 to form two more Ag atoms and two NH_4^+ ions during the sorption and reaction steps. Two NH_4^+ cations have been located at N(5) in the small cubic cavity, a novel site, where they form suitable hydrogen bonds to the zeolite framework: N(5)-O(1) = 2.59 (5) N(5)-O(3) = 2.7 (7) Å (see Table I, footnote *g*). Experiments designed to isolate N_3H_3 and N_3H_5 in pure form are in progress.

Acknowledgments. This work was supported by the National Science Foundation (Grant No. CHE73-08761). We are indebted to the University of Hawaii Computing Center.

Supplementary Material Available: A listing of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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Received February 25, 1977

Near-Zero-Coordinate, Three-Coordinate, and Four-Coordinate Europium(II). Bonding Effects Involving Europium(II) Valence Orbitals. Crystal Structure of Dehydrated Near-Fully Europium(II)-Exchanged Zeolite A

Sir:

The structures of a number of zeolite A crystals which have been incompletely exchanged with divalent cations show that these cations are all located at 6-ring[1] sites. This is true for Ca_4Na_4-A[2,3] and other structures containing Mn(II),[4,5] Co(II),[5,6] and Zn(II).[5,7] It was anticipated that divalent cations is more completely exchanged zeolite A structures, $M_x{}^{2+}Na_{12-2x}$-A, $5 \leq x \leq 6$, would also all locate at 6-ring sites. This expectation is now shown to be incorrect. In dehydrated Eu_xNa_{12-2x}-A, where x is ~5.75, one Eu(II) ion per unit cell is located in the plane of an 8-ring, surprisingly at a site of near-zero coordination.

Zero coordinate and near-zero coordinate monovalent cations have been well documented crystallographically in zeolite A,[8-12] and the principles governing their existence have been discussed.[9,10,12] Somewhat different principles describe the near-zero coordination of divalent ions. To learn more about these principles, and to further support this work with Eu(II), the crystal structures of dehydrated Ca_6-A and Sr_6-A have subsequently been determined.[13] In both, one near-zero-coordinate cation per unit cell is found at an 8-ring site. In Ca_6-A and Sr_6-A, the near-zero-coordinate Ca^{2+} and Sr^{2+} ions are 0.77 and 0.52 Å farther, respectively, from the nearest framework oxide ions (two O(1)s and one O(2); see Figure 1) than the sum of the appropriate ionic radii[14] would indicate. The corresponding discrepancy reported here for Eu(II) is 0.96 Å. This last result is particularly reliable because of the large scattering factor of Eu(II) for x rays.

A single crystal of sodium zeolite 4A, Na_{12}-A, 0.09 mm on an edge, was lodged in a fine glass capillary. $Eu(OH)_2$ was synthesized by the method of Bärnighausen[15] under anoxic conditions. Ion exchange was performed in the dark under nitrogen by allowing a saturated aqueous solution of $Eu(OH)_2$ to flow past the crystal at nearly 1.0 mm/s for 3 days. The crystal, whose appearance was not altered by this exchange procedure, was then dehydrated for 48 h at 350 °C and 5×10^{-6} Torr. Microscopic examination indicated that the crystal was still clear and undamaged, but that it had developed a bright orange color. It is considered unlikely that any Eu(II) was oxidized in any way, including by reaction with water, to form Eu(III); in fact, the reverse has been demonstrated intrazeolitically.[16]

The space group *Pm*3*m* (no systematic absences) was used throughout this work for reasons discussed previously.[1a] The structure, $a = 12.296$ (2) Å at 23 (1) °C, was solved using 370 unique observed ($I_0 > 3\sigma(I_0)$; $3° < 2\theta < 70°$) reflections collected by counter methods using a fully automated Syntex $P\bar{1}$ diffractometer with monochromatic Mo Kα radiation (Kα_1, $\lambda = 0.70930$ Å; Kα_2, $\lambda = 0.71359$ Å) and a pulse-height analyzer. Other experimental details including data reduction are the same as previously presented.[7] The unit cell composition as determined by refinement of the diffraction data is $Eu_xNa_{12-2x}Si_{12}Al_{12}O_{48}$, where x is 5.75 ± 0.25; 6.0 is the maximum value, corresponding to complete exchange. This dehydrated material will subsequently be referred to as Eu-A.

Least-squares refinement[17] of Eu-A began using the atomic parameters of the atoms of the aluminosilicate framework: (Si, Al), O(1), O(2), and O(3).[18] In addition, a probable Eu(II) position at Eu(1) (see Table I), in the large cavity near the planes of the 6 rings, was included. A subsequent Fourier difference function revealed the presence of a Eu(II) ion at Eu(2) in the sodalite unit, and a peak ~5.7 e Å^{-3} in height at (0,½,½). This peak, at the center of the 8 ring, was stable in least-squares refinement as one Eu(II) ion at Eu(3). An ion at Eu(4) was located on a subsequent electron density difference function. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement of all Eu(II) ions resulted in an R_2 index of 0.112 and occupancies very near those shown in Table I. These occupancy parameters placed 3.19 (9) ions at Eu(1), 0.79 (6) ions at Eu(2), 0.96 (5) ions at Eu(3), and 0.74 (10) ions at Eu(4). By the assumption of stoichiometry, the first three values were rounded to the integers 3, 1, and 1, respectively. The occupancy of Eu(4) was fixed at 0.75 ions per unit cell because the error indices rose somewhat when one full ion was placed there, even though the thermal parameters were allowed to adjust. Anisotropic refinement of all atoms at the occupancies shown in Table I quickly converged to an R_2 weighted index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o{}^2)^{1/2}$, of 0.114 ($R_1 = 0.135 = \Sigma|F_o - |F_c||/\Sigma F_o$). A trial removal of Eu(3), the near-zero-coordinate cation, from least-squares