Crystallographic Studies of Dehydrated Ag^+ and K^+ Exchanged Zeolite A Reacted with Alkali Metal Vapor

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The crystal structure of dehydrated $Ag_{5.6}K_{6.4}$-A, zeolite A ion-exchanged with K^+ and Ag^+ as indicated and dehydrated at 360℃, has been determined by single-crystal X-ray diffraction techniques. Also determined were the structures of the products of the reactions of this zeolite with 0.1 Torr of Cs vapor at 250℃ for 48 h and 72 h, and with 0.1 Torr of Rb vapor at 250℃ for 24 h. The structures were solved and refined in the cubic space group $Pm3m$ at 21(1) ℃ (a=12.255(1) Å, 12.367(1) Å, 12.350(1) Å, and 12.263(1) Å, respectively). Dehydrated $Ag_{5.6}K_{6.4}$-A was refined to the final error indices $R_1=0.044$ and $R_2=0.037$ with 202 reflections for which $I>3\sigma(I)$. The crystal structures of the reaction products were refined to $R_1=0.087$ and $R_2=0.089$ with 157 reflections, $R_1=0.080$ and $R_2=0.087$ with 161 reflections, and $R_1=0.071$ and $R_2=0.061$ with 88 reflections, respectively. In the structure of $Ag_{5.6}K_{6.4}$-A, K^+ ions block all 8-oxygen rings, and one reduced Ag atom is found per sodalite cavity. Also, *ca.* 4.6 Ag^+ ions and 3.4 K^+ ions are found at 6-ring sites in the large cavity. The crystal structures of the reaction products show that all K^+ and Ag^+ ions have been reduced, and that all K atoms have left the zeolite. Cs or Rb species are found at three different crystallographic sites: 3.0 Cs^+ or 3.0 Rb^+ ions per unit cell occupy 8-ring centers, *ca.* 8.0 Cs^+ ions or 5.7 Rb^+ ions, are found on threefold axes opposite 6-rings deep in the large cavity, and *ca.* 2.5 Cs^+ or 2.3 Rb^+ ions are found on threefold axes in the sodalite unit. Also, 1 Rb^+ ion lies opposite a 4-ring. Silver atoms, corresponding to 75% or 40% occupancy of hexasilver clusters stabilized by coordination to Cs^+ or Rb^+ ions, are found at the centers of the large cavities. In the crystal structures of dehydrated $Ag_{5.6}K_{6.4}$-A reacted with Cs vapor, excess Cs atoms are absorbed and these form (locally) cationic clusters such as $(Cs_4)^{3+}$ and $(Cs_6)^{4+}$.

Introduction

Silver ions can be reduced intrazeolitically be heating,[1,2] by reaction with reducing agents,[3] or by sorption of metal atoms.[4] Tsutsumi and Takahashi reported that the Ag^+ ions in zeolite Y can be reduced to bulk clusters of Ag^0 after treatment with alcohol and alkyl benzene above 300℃.[5] Several crystal structures of fully Ag^+-exchanged zeolite A have been determined. Fully dehydrated Ag_{12}-A contains silver atoms, probably as hexasilver molecules centered within some of its sodalite cavities.[1,2] Hermerschmit and Haul identified uncharged silver clusters, $(Ag_6)^0$, in dehydrated Ag^+-exchanged zeolite A by using EPR spectroscopy[6] and their results were duplicated by Grobet and Schoonheydt.[7] This was reverified by the careful work of Morton and Preston on Ag-A using isotopically pure silver.[8] These clusters, $(Ag_6)^0$, stabilized by coordination to eight Ag^+ ions, may also be viewed as $(Ag_{14})^{8+}$. Subsequently, the silver clusters $(Ag_5)^{4+}$, $(Ag_3)^+$, $(Ag_3)^{2+}$ and $(Ag_6)^{3+}$ were identified in partially Ag^+-exchanged zeolite A which had been treated with H_2.[3,9]

Barrer *et al.* reported that about 45% of Na^+ ions in zeolite A could be replacd by Cs^+ ions by a static ion-exchange method.[10] Later Dejsupa *et al.* prepared Cs_{12}-A·CsOH by the reaction of a single crystal of hydrated $(NH_4^+)_{12}$-A with a modest excess of CsOH slush.[11] Recently fully Cs^+-exchanged zeolite A has been synthesized by the reduction of all Na^+ ions in Na_{12}-A by Cs vapor. The redox reaction goes to completion 350℃ with 0.1 Torr of Cs to give Cs_{12}-A·0.5Cs. In that structure, the extra Cs atom associated with two or three Cs^+ ions to form linear $(Cs_3)^{2+}$ or $(Cs_4)^{3+}$ clusters.[12,13]

Rb^+ ions, like Cs^+ ions, are large and monopositive, and also exchanged only incompletely (about 90%) into zeolite A by flow methods.[14,15] Fully dehydrated fully Rb^+-exchanged zeolite A single crystals have been prepared by reaction of Na_{12}-A with rubidium vapor. In these structures, 12.6(2) to 13.5(2) Rb ions and/or atoms ard found per unit cell, more than the 12 Rb^+ ions needed to balance the anionic charge of the zeolite framework.[16] The structural analysis indicated that each of three Rb species in the sodalite cavity bond to an Rb species in the large cavity to give an $(Rb_6)^{4+}$ cluster.

This work was done with the hope that Cs and Rb vapor would reduce the Ag^+ and K^+ ions in zeolite A to form Ag atoms and clusters which might be examined crystallographically. The ions in the resulting structures should be readily distinguishable because they have a broad range of scattering factors (approximately proportional to their atomic numbers) and ionic radii (Ag^+=1.26 Å, K^+=1.33 Å, Rb^+= 1.47 Å, and Cs^+=1.67 Å[17]). Highly dispersed metal clusters are important because they are used as catalysts in hydrogenation and oxidation reactions.

Experimental Section

Crystals of synthetic molecular sieve zeolite 4A were prepared by Charnell's method.[18] Three crystals of composition $Ag_{5.6}K_{6.4}$-A were prepared by using an exchange solutions whose $AgNO_3:KNO_3$ mole ratio was 1 : 1000 with total concentration of 0.05 M. Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 0.5 cm/s for 3 days at 25(1)℃. Each crystal was dehydrated at 360℃ and 2×10^{-6} Torr for 2 days. One single crystal (crystal 1) was sealed in its capillary by a torch, still under vacuum, after dehydration; it had become red. Cs or Rb vapor was introduced to the remaining three crystals be distillation from a side-arm break-seal ampule to the Pyrex-tube extension of each crystal-containing capillary. Each Pyrex reaction vessel was then sealed off under vacuum and placed in a pair of cylindrical horizontal ovens, axes collinear, attached. The oven about the crystal was alway maintained at a higher temperature than that about the metal so that the cesium or rubidium vapor would not distill onto the crystal. In the preparation of crystal 2, Cs(g) at 0.1 Torr (the vapor pressure of Cs(l) at 210℃) was allowed to react with $Ag_{5.6}K_{6.4}$-A at 250℃ for 48 h. Crystal 3 was treated like the second but for a longer time, 72 h. Crystal 4 was treated with 0.1 Torr of Rb(g) (the vapor pressure of Rb(l) at 220℃) at 250℃ for 24 h. Each crystal was sealed off from its reaction vessel by torch after cooling to room temperature. Microscopic examination showed that all three crystals had become black.

The cubic space group *Pm*3*m* (no systematic absences) was used for reasons discussed previously.[19,20] Diffraction data were collected at 21(1)℃ with an automated Enraf-Nonius four-circle computer-controlled diffractometer with a graphite monochromator, using Mo Kα radiation (Kα_1, $\lambda=0.70930$ Å, Kα_2, $\lambda=0.71359$ Å). The cubic unit cell constants, as determined by a least-squares refinement of 25 intense reflections for which $19° < 2\theta < 25°$ are $a=12.255(1)$ Å, 12.367(1) Å, 12.350 (1) Å, and 12.263(1) Å for crystals 1, 2, 3, and 4, respectively.

Reflections from two intensity-equivalent regions of reciprocal space (*hkl*, $h \leq k \leq l$; *hlk*, $h \leq l \leq k$) were examined using the ω-2θ scan technique. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.11° and 0.41° in ω min^{-1}. The intensities of three reflection in diverse regions of reciprocal space were recorded every three hours to monitor crystal and X-ray source stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70°$ were recorded.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviations were assigned to each averaged reflection by the computer programs, PAINT and WEIGHT.[21] An absorption correction[22] ($\mu R = 0.088$, 0.311, 0.323, and 0.328 for crystals 1, 2, 3, and 4, respectively) was not applied. Of the 874, 893, 891, and 874 pairs of reflections for crystals 1, 2, 3, and 4, respectively, only the 202, 157, 161, and 88 pairs, respectively, for which $I > 3\sigma(I)$ were used in subsequent structure determinations.

Structure Determination

Crystal 1 (dehydrated $Ag_{5.6}K_{6.4}$-A). Full-matrix least-squares refinement was initiated with the atomic parameters of the framework atoms [(Si, Al), O(1), O(2), and O(3)], Ag^+ ions at Ag(1), and K^+ ions at K(1) of dehydrated $Ag_{9.3}K_{2.7}$-A.[23] Anisotropic refinement converged to an unweighted R_1 index, $\Sigma(|F_o - |F_c||)/\Sigma F_o$, of 0.075 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$, of 0.079. A difference Fourier synthesis revealed the positions of Ag species at Ag(2), (0, 0, 0.17), with peak height 4.9(3) $e\text{Å}^{-3}$, and K^+ ions at K(2), (0.25, 0.25, 0.25), with peak height 2.3(3) $e\text{Å}^{-3}$. Both peaks were refined by least-squares. The occupancies obtained were reset and fixed as in Table 1 for chemical reasons. The final difference function was featureless except for one peak at (0.0, 0.5, 0.5) with peak height 1.6(4) $e\text{Å}^{-3}$. This peak was too close to the K^+ ion at K(1) and was not considered further. The final error indices were $R_1 = 0.044$ and $R_2 = 0.037$.

Crystal 2 (dehydrated $Ag_{5.6}K_{6.4}$-A treated with 0.1 Torr of Cs(g) at 250°C for 48 h). Initial full-matrix least-squares refinement of the structure was carried out using the atomic framework parameters of dehydrated $Ag_{5.6}K_{6.4}$-A. Anisotropic refinement of the framework atoms converged to $R_1 = 0.51$ and $R_2 = 0.64$. A subsequent difference Fourier revealed three large peaks: (0.0, 0.5, 0.5), height 4.1 (3) $e\text{Å}^{-3}$; (0.28, 0.28, 0.28), 10.9(2) $e\text{Å}^{-3}$; and (0.11, 0.11, 0.11), 6.9(2) $e\text{Å}^{-3}$. Anisotropic refinement of the framework atoms and Cs^+ ions at Cs(1), Cs(2), and Cs(3) converged to R_1 and R_2 indices of 0.139 and 0.157, respectively (see Table 1). The ensuing difference Fourier revealed two peaks at (0.33, 0.5, 0.5) and (0.25, 0.25, 0.5) with heights of 6.8(3) $e\text{Å}^{-3}$ and 1.2(3) $e\text{Å}^{-3}$, respectively. The first peak was refined and designated Ag(1), and the second peak was unstable in least-squares refinement with an unusually large thermal parameter. This peak was also too close to Cs^+ ions at Cs(2), so it was deleted. Simultaneous positional, thermal, and occupancy refinement, except the occupany as Cs(1) which was not permitted to exceed 3.0 (its maximum occupancy), refin-

Table 1. Positional, Thermal,[a] and Occupancy Parameters of Crystal 1,[b] Crystal 2,[c] Crystal 3,[d] and Crystal 4.[e]

Crystal 1.

Atom	Wyc. Pos.	*x*	*y*	*z*	β_{11}[f]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[g]	
											varied	fixed
(Si,Al)	24(*k*)	0	1845(2)	3729(2)	24(2)	20(2)	13(1)	0	0	2(4)		24.0[h]
O(1)	12(*h*)	0	2273(8)	5000	56(9)	58(9)	25(7)	0	0	0		12.0
O(2)	12(*i*)	0	2929(5)	2929(5)	57(8)	27(4)	27(4)	0	0	40(10)		12.0
O(3)	24(*m*)	1122(4)	1122(4)	3450(6)	36(3)	36(3)	60(6)	30(10)	−6(7)	−6(7)		24.0
Ag(1)	8(*g*)	1928(2)	1928(2)	1928(2)	67(1)	67(1)	67(1)	100(2)	100(2)	100(2)	4.59(2)	4.60
Ag(2)	6(*e*)	0	0	1690(20)	50(10)	50(10)	50(30)	0	0	0	0.40(8)	1.00
K(1)	12(*i*)	0	4628(8)	4628(8)	160(20)	80(10)	80(10)	0	0	−20(20)	2.85(5)	3.00
K(2)	8(*g*)	2260(9)	2260(9)	2260(9)	152(5)	152(5)	152(5)	240(10)	240(10)	240(10)	3.41(6)	3.40

Crystal 2.

Atom	Wyc. Pos.	x	y	z	β_{11}[f]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[h] varied	Occupancy[h] fixed
(Si,Al)	24(*k*)	0	1840(9)	3722(9)	14(6)	6(7)	6(6)	0	0	10(10)		24.0[h]
O(1)	12(*h*)	0	2310(30)	5000	130(60)	−20(30)	30(30)	0	0	0		12.0
O(2)	12(*i*)	0	2860(20)	2860(20)	30(30)	20(10)	20(10)	0	0	50(60)		12.0
O(3)	24(*m*)	1120(10)	1120(10)	3500(20)	60(20)	60(20)	20(20)	−30(40)	10(30)	10(30)		24.0
Cs(1)	3(*c*)	0	5000	5000	130(10)	55(6)	55(6)	0	0	0	3.24(6)	3.0
Cs(2)	8(*g*)	2806(4)	2806(4)	2806(4)	78(2)	78(2)	78(2)	23(7)	23(7)	23(7)	7.58(7)	7.6
Cs(3)	8(*g*)	1100(7)	1100(7)	1100(7)	31(6)	31(6)	31(6)	0(10)	0(10)	0(10)	2.28(7)	2.4
Ag(1)	6(*f*)	3430(30)	5000	5000	360(50)	360(30)	360(30)	0	0	0	4.40(12)	4.5

Crystal 3.

Atom	Wyc. Pos.	x	y	z	β_{11}[f]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[h] varied	Occupancy[h] fixed
(Si,Al)	24(*k*)	0	1836(9)	3734(9)	21(7)	19(7)	7(7)	0	0	0(1)		24.0[i]
O(1)	12(*h*)	0	2280(30)	5000	130(50)	0(3)	20(30)	0	0	0		12.0
O(2)	12(*i*)	0	2890(20)	2890(20)	30(30)	20(20)	20(20)	0	0	−10(60)		12.0
O(3)	24(*m*)	1120(10)	1120(10)	3490(20)	50(10)	50(10)	10(20)	−10(40)	10(30)	10(30)		24.0
Cs(1)	3(*c*)	0	5000	5000	140(10)	60(6)	60(6)	0	0	0	3.30(6)	3.0
Cs(2)	8(*g*)	2796(3)	2796(3)	2796(3)	74(2)	74(2)	74(2)	18(7)	18(7)	18(7)	8.24(8)	8.0
Cs(3)	8(*g*)	1097(8)	1097(8)	1097(8)	33(6)	33(6)	33(6)	−20(10)	−20(10)	−20(10)	2.53(7)	2.5
Ag(1)	6(*f*)	3480(30)	5000	5000	310(20)	270(20)	270(20)	0	0	0	4.39(10)	4.5

Crystal 4.

Atom	Wyc. Pos.	x	y	z	β_{11}[f] or β_{iso}[g]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy[h] varied	Occupancy[h] fixed
(Si,Al)	24(*k*)	0	1833(8)	3727(7)	40(6)	32(7)	18(7)	0	0	0(2)		24.0[i]
O(1)	12(*h*)	0	2250(20)	5000	50(30)	70(30)	40(30)	0	0	0		12.0
O(2)	12(*i*)	0	2890(20)	2890(20)	50(30)	50(20)	50(20)	0	0	40(50)		12.0
O(3)	24(*m*)	1110(10)	1110(10)	3480(20)	80(10)	80(10)	40(20)	50(40)	−0(30)	−0(30)		24.0
Rb(1)	3(*c*)	0	5000	5000	210(30)	240(20)	240(20)	0	0	0	2.75(6)	3.0
Rb(2)	8(*g*)	2687(5)	2687(5)	2687(5)	94(5)	94(5)	94(5)	60(10)	60(10)	60(10)	5.72(9)	5.7
Rb(3)	8(*g*)	1140(10)	1140(10)	1140(10)	90(10)	90(10)	90(10)	−10(30)	−10(30)	−10(30)	2.36(7)	2.3
Ag(1)	6(*f*)	3450(20)	5000	5000	230(40)	170(20)	170(20)	0	0	0	2.29(6)	2.4
Ag(2)	12(*j*)	2400(50)	2400(50)	5000	12(3)						0.93(10)	1.0

[a] Positional and anisotropic thermal parameters are given ×10^4. Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. [b] All Na^+ ions of zeolite 4A are exchanged by Ag^+ and K^+. [c] $Ag_{5.6}K_{6.4}$-A treated with 0.1 Torr of Cs vapor at 250℃ for 48 h. [d] $Ag_{5.6}K_{6.4}$-A treate with 0.1 Torr of Cs vapor at 250℃ for 72 h. [e] $Ag_{5.6}K_{6.4}$-A treated with 0.1 Torr of Rb vapor for 24 h. [f] The anisotropic temperature factor=$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl)]$. [g] Isotropic thermal parameters in units of Å^2. [h] Occupancy factors are given as the number of atoms or ions per unit cell. [i] Occupancy for (Si)=12; occupancy for (Al)=12.

ed to $R_1=0.087$ and $R_2=0.086$ (see Table 1). The occupancies obtained were reset and fixed as in Table 1 for chemical considerations. The final error indices were $R_1=0.087$ and $R_2=0.089$. The final difference function was featureless except for one peak at (0.0, 0.5, 0.5) with peak height 1.9(7) eÅ^{-3}, residual electron density at Cs(1). The final structural parameters are presented in Table 1. All shifts in the final cycle of least-squares were less than 0.2% of their corresponding esd's.

Crystal 3 (dehydrated $Ag_{5.6}K_{6.4}$-A treated with 0.1 Torr of Cs(g) at 250°C for 72 h). Full-matrix least-squares refinement began with the atomic coordinates of crystal 1. Anisotropic refinement of framework atoms converged to $R_1=0.54$ and $R_2=0.68$, A difference Fourier revealed three peaks at Cs(1), Cs(2) and Cs(3) of height of 5.3(3), 13.2(2), and 6.8(2) eÅ^{-3}. Anisotropic refinement of the framework atoms and Cs^+ ions converged to $R_1=0.15$ and $R_2=0.19$. A subsequent difference Fourier revealed a peak of height 10.6(3) eÅ^{-3} at (0.34, 0.5, 0.5) which was stable in least-squares refinement. The occupancies obtained were reset within three esd's and fixed as in Table 1 for chemical considerations. Simultaneous positional and anisotropic thermal parameter refinement converged to the final error indices $R_1=0.080$ and $R_2=0.089$. The final difference Fourier

Table 2. Selected Interatomic Distances (Å) and Angles (deg)

	Crystal 1		Crystal 2	Crystal 3		Crystal 4
(Si,Al)-O(1)	1.64(1)		1.69(2)	1.66(2)		1.64(1)
(Si,Al)-O(2)	1.65(1)		1.65(2)	1.67(2)		1.65(2)
(Si,Al)-O(3)	1.67(1)		1.67(1)	1.67(1)		1.66(1)
K(1)-O(1)	2.92(1)	Cs(1)-O(1)	3.32(4)	3.35(4)	Rb(1)-O(1)	3.37(3)
K(1)-O(2)	2.95(1)	Cs(1)-O(2)	3.74(2)	3.67(2)	Rb(1)-O(2)	3.65(1)
K(2)-O(3)	2.45(1)	Cs(2)-O(3)	3.06(1)	3.05(1)	Rb(2)-O(3)	2.91(1)
		Cs(3)-O(3)	2.97(3)	2.96(3)	Rb(3)-O(3)	2.88(2)
		Ag(1)-O(1)	5.39(4)	5.44(3)	Ag(1)-O(1)	5.41(3)
		Ag(1)-O(2)	5.66(3)	5.66(3)	Ag(1)-O(2)	5.59(2)
Ag(1)-O(3)	2.33(1)	Cs(1)-Cs(2)	5.17(1)	5.17(1)	Ag(2)-O(1)	2.95(6)
Ag(2)-O(3)	2.91(2)				Ag(2)-O(3)	2.91(4)
		Ag(1)-Ag(1)	2.75(4)	2.65(3)	Ag(1)-Ag(1)	2.68(3)
Ag(1)-Ag(2)	3.36(1)				Ag(1)-Ag(2)	3.35(2)
Ag(2)-Ag(2)	2.92(3)	Cs(3)-Cs(3)	2.72(1)	2.71(1)		
			3.86(1)	3.83(1)		
		Ag(1)-Cs(1)	4.24(4)	4.30(3)	Rb(1)-Rb(2)	5.19(1)
		Ag(1)-Cs(2)	3.91(1)	3.94(1)	Ag(1)-Rb(2)	4.12(1)
		Cs(2)-Cs(3)	3.66(1)	3.63(1)		
					Rb(2)-Rb(3)	3.29(2)
					Rb(3)-Rb(3)	3.95(1)
O(1)-(Si,Al)-O(2)	107.8(4)		110(10)	109(1)		111(1)
O(1)-(Si,Al)-O(3)	111.3(3)		110(1)	110(1)		109.9(9)
O(2)-(Si,Al)-O(3)	107.8(3)		107.4(9)	107.6(8)		108.2(7)
O(3)-(Si,Al)-O(3)	110.8(2)		112.7(8)	111.9(9)		110.6(8)
(Si,Al)-O(1)-(Si,Al)	142.7(7)		139(2)	141(2)		144(2)
(Si,Al)-O(2)-(Si,Al)	162.8(3)		170(1)	167(1)		166(1)
(Si,Al)-O(3)-(Si,Al)	146.1(4)		149(1)	148(1)		149(1)
O(3)-Ag(1)-O(3)	119.9(1)	O(3)-Cs(2)-O(3)	85.4(6)	85.5(5)	O(3)-Rb(2)-O(3)	90.3(4)
O(1)-K(1)-O(2)	54.0(2)					
O(3)-K(2)-O(3)	110.7(1)	O(3)-Cs(3)-O(3)	88.8(3)	88.9(3)	O(3)-Rb(3)-O(3)	91.6(3)
Ag(1)-Ag(2)-Ag(1)	89.56(9)	Ag(1)-Cs(1)-Ag(1)	180(0)	180(0)	Ag(1)-Rb(1)-Ag(1)	180.1(5)

function was featureless except for one small peak, 1.3(3) eÅ^{-3} in height at (0.23, 0.23, 0.5). This position was too close to Cs$^+$ ions at Cs(1) and refined to an unusually large thermal parameter, so it was deleted.

Crystal 4 (dehydrated $Ag_{5.6}K_{6.4}$-A treated with 0.1 Torr of Rb(g) at 250°C for 24 h). Full-matrix least-squares refinement began with the atomic parameters of the framework atoms of crystal 2. Anisotropic refinement of framework atoms converged to $R_1=0.47$ and $R_2=0.60$. A subsequent difference Fourier function revealed three peaks at Rb(1), Rb(2), and Rb(3) with heights 1.9(2), 10.0(2), and 6.8(2) eÅ^{-3}, respectively (see Table 1). Anisotropic refinement of the framework atoms and of Rb$^+$ ions at Rb(1), Rb(2), and Rb(3) converged to $R_1=0.26$ and $R_2=0.24$. An ensuing difference Fourier revealed the positions of Ag atoms (0.34, 0.5, 0.5), peak height 4.0(3) eÅ^{-3}, and Rb$^+$ ions at Rb (4), (0.24, 0.24, 0.5), height 1.5(2) eÅ^{-3}. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement, except for that of Rb(4), which was refined isotropically, converged to $R_1=0.071$ and $R_2=0.061$. The final difference function was featureless except for one small peak, 1.5(3) eÅ^{-3} in height at (0, 0, 0.416) in the large cavity. This peak was unstable in least-squares and was discarded.

For all structures, the computer program used for least-squares refinement minimized the quantity $\Sigma w(F_o-|F_c|)^2$ where *w*, the weight of an observation, was the reciprocal square of its estimated standard deviation, $\sigma(F_o)$. Atomic scattering factors for Ag$^+$, Ag^0, K$^+$, Cs$^+$, Rb$^+$, O$^-$, and (Si, Al)$^{1.75+}$ (the average of Si^0, Si^{4+}, Al^0, and Al^{3+}) were used.[24] All atomic scattering factors were modified to account for anomalous dispersion.[25] The final structural parameters and selected interatomic distances and angles are presented in Tables 1 and 2, respectively.

Discussion

Dehydrated $Ag_{5.6}K_{6.4}$-A. In this structure, Ag$^+$ ions Ag (1) and K$^+$ ions at K(2) are on threefold axes of the unit cell and associate with 6-ring oxygens[26] (Figure 1). These positions had been found previously.[23] At Ag(1), 4.60 Ag$^+$ ions are 2.33(1) Å from three O(3)'s, less than the sum of Ag$^+$ and O^{2-} radii, 2.58 Å. The Ag(1)-O(3) bonds therefore have substantial convalent character. The O(3)-Ag(1)-O(3) angle of 119.9(1)° indicates that Ag(1) has achieved trigonal-planar coordination (see Tables 2 and 3).

Also on threefold axes are 3.4 K$^+$ ions at K(2). These

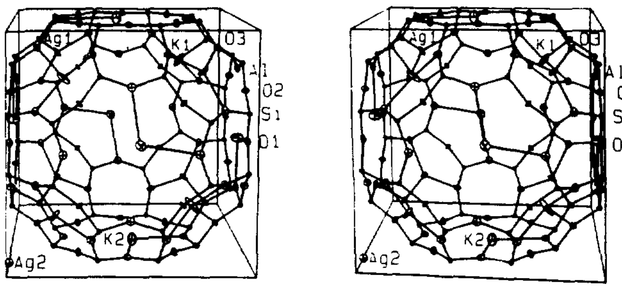

Figure 1. A stereoview of the large cavity of dehydrated $Ag_{5.6}K_{6.4}$-A. Ellipsoids of 20% probability are used.

Table 3. Deviations of Atoms (Å) from the (111) Plane at O (3)^a

	Crystal 1		Crystal 2	Crytal 3		Crystal 4
K(1)	0.77	Cs(2)	1.91	1.90	Rb(2)	1.68
		Cs(3)	−1.75	−1.74	Rb(3)	−1.61
Ag(1)	0.06	Ag(1)	5.50	5.53	Ag(1)	5.50
O(2)	0.12		0.06	0.02		0.04

^{a}A negative deviation indicates that the atom lies on the same side of the plane as the origin.

are recessed 0.77 Å into the large cavity from the (111) plane at O(3) (see Table 3). Each of these K^+ ions coordinates to three O(3) oxygens at 2.45(1) Å, somewhat less than the sum of K^+ and O^{2-} radii, 2.65 Å.[17] The actual O(3) coordinates in a K^+-containing 6-ring must be different from those in an Ag^+-containing 6-ring, and this must lead to inaccuracies in both Ag^+-O(3) and K^+-O(3) bond lengths. The former are likely to be shorter than herein reported, and the latter longer.

Three K^- ions at K(1) lie in 8-ring planes, but not at 8-ring centers. They approach two framework O(1) oxygens and one O(2) oxygen at 2.92(1) and 2.95(1) Å, respectively. These distances are substantially longer than the sum of the ionic radii. Such long interaction distances have been observed previously in other zeolite A structures.[23]

The distance between Ag(2) and O(3) is long, 2.91(2) Å (see Table 2). This Ag position is very similar to that of the silver atoms of hexasilver in the structure of dehydrated partially decomposed Ag_{12}-A.[1,2] The 3.36(1) Å distance between Ag(1) and Ag(2) is too short to be an unmoderated Ag^+-Ag^+ contact, and too long to be an Ag^0-Ag^0 bond. The Ag(1)-Ag(2) distance may, however, be viewed as an Ag^0-Ag^+ coordination contact distance. The shortest possible Ag(2)-Ag (2) distance, 2.92(3) Å, is about the same as the Ag-Ag atom distance in silver metal, 2.889 Å.[27] Therefore, the Ag species at Ag(2) are not Ag^+ ions but reduce Ag atoms.

In this structure, K^+ ions preferentially occupy 8-ring sites and Ag^+ ions occupy 6-ring sites. This result is consistent with the ionic radii K^- (1.33 Å) and Ag^+ (1.26 Å). This result had been seen before in the structures of Ag_9Cs_3-A[28] and Ag_9Rb_3-A.[29] In each, the three Cs^- and three Rb^+ ions are found at 8-ring centers.

Crystals 2 and 3, approximate compositions $Cs_{13.5}Ag_{4.5}$-A. Upon reaction of vacuum-dehydrated $Ag_{5.6}K_{6.4}$-A with 0.1 Torr of Cs vapor at 250℃ for 48 h, all K^+ and Ag^+ ions were reduced and replaced by Cs^+ ions. All K and some Ag atoms have left the zeolite.

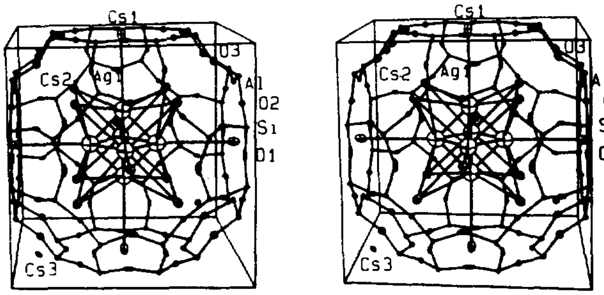

Figure 2. A stereoview of the large cavity containing an Ag_6 molecule. The octahedral Ag_6 molecule is stabilized by coordination to 6 Cs^+ ions at Cs(1) and 8 Cs^+ ions at Cs(1). Ellipsoids of 20% probability are used.

Cs^+ ions are found at three different crystallographic sites, and Ag species are found at only one site. At Cs(1), three Cs^+ ions fill the equipoints of symmetry D_{4h} at the centers of the 8-rings, as they have in all previously reported Cs^+-exchanged zeolite A structures. Each Cs(1) ion is *ca.* 3.34(3) Å from four O(1) oxygens and *ca.* 3.70(2) Å from four O(2)'s (see Table 2). These distances are substantially longer than the sum of the ionic radii of O^{2-} and Cs^+, 2.99 Å. Theoretical calculations support this observation of a potential energy minimum at these positions.[30,31]

In the large cavity opposite 6-rings, *ca.* 7.6 Cs^+ ions for crystal 2 and *ca.* 8.0 Cs^+ ions for crystal 3 are found at Cs(2) (see Table 2). These extend 1.90 Å into the large cavity from the (111) plane at O(3) and coordinate to three O(3) oxygens of the 6-ring at 3.06(1) Å.

About 4.5 Ag atoms at Ag(1), the products of the reduction of Ag^+ by Cs^0, are located near the center of the large cavity. The distance between Ag(1) and its nearest framework oxygens, four at O(1), is very much longer (Ag(1)-O(1)=5.42(2) Å) than the sum of the corresponding ionic radii, 2.58 Å. This indicates that the species at Ag(1) must be Ag^0 and not Ag^+. The shortest Ag(1)-Ag(1) distance, *ca.* 2.70(5) Å which must exist whenever three more silver species are present at Ag(1) per unit cell, is far too short to be an unmoderated Ag^+-Ag^+ contact distance and must be an Ag^0-Ag^0 contact. This short distance was also found in previous work on the crystal structures of dehydrated Ag^+- and Ca^{2+}-exchanged zeolite A treated with Rb vapor.[32] Ag species at Ag(1) are likely to have formed hexasilver clusters at the centers of the large cavities as in previous work.[32] If the Ag(1) equipoint is filled in a fraction of the large cavities, as is sensible to infer but not proven solely by these crystallographic results, closest-packed clusters of six silver atoms would exist at the centers of about 75% of the large cavities (see Figure 2). The hexasilver molecule would be octahedral and would show the full symmetry of its site, O_h, at the center of the large cavity. The structure and symmetry of this hexasilver cluster is exactly the same as that found at the center of the sodalite unit in partially decomposed, fully dehydrated Ag^+-exchanged zeolite A.[1,2] The relatively large thermal ellipsoids of the Ag atoms at Ag(2) indicate that the hexasilver cluster is loosely held. It is stabilized by association with 8 Cs^+ ions at Cs(2) and 6 Cs^+ ions at Cs(1)

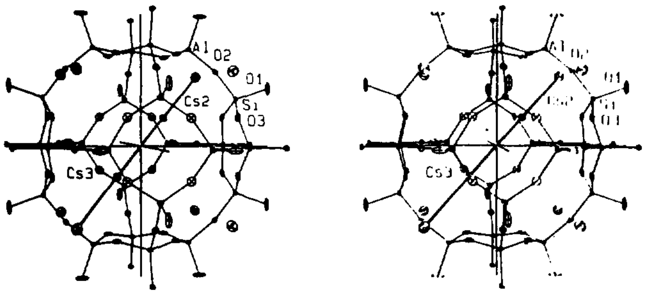

Figure 3. A stereoview of about half of sodalite units of Ag$_{4.5}$Cs$_{13.5}$-A. A linear (Cs$_4$)$^{4+}$ cluster is shown. Ellipsoids of 20% probability are used.

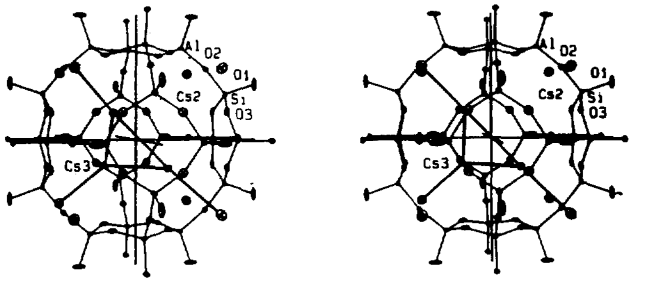

Figure 4. The remaining half of the sodalite cavities in Ag$_{4.5}$Cs$_{13.5}$-A may have this arrangement. Each Cs(3) of the central triangle of the cluster interacts further with cesium at Cs(2) to form the complete (Cs$_6$)$^{4+}$ cluster. Ellipsoids of 20% probability are used.

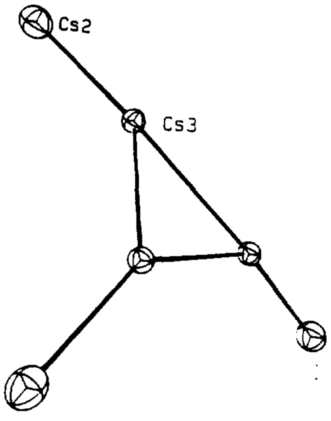

Figure 5. The (Cs$_6$)$^{4+}$ cluster, symmetry $3m$ (C_{3v}). Ellipsoids of 20% probability are used.

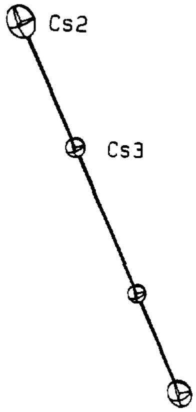

Figure 6. A close-up view of the (Cs$_4$)$^{3+}$ cluster. Ellipsoids of 20% probability are used.

(Cs(1)-Ag(1)=4.27(4) Å and Cs(2)-Ag(1)=3.92(1) Å) (see Figure 2).

About 2.5 Cs$^+$ ions at Cs(3), also on threefold axes and associated with 6-rings, are recessed *ca.* 1.74 Å into the sodalite cavity from the (111) plane at O(3). Each of these ions coordinates to three O(3) oxygens at 2.97(2) Å (see Figure 3).

In crystal 3, the fractional occupancy at Cs(3) indicates the existence of two types of sodalite units. About 50% of sodalite units may have two Cs species at Cs(3) and the remaining 50% may have three (Other distributions, including some to form tetracesium clusters, are considered less likely). Sodalite units with three Cs(3)'s must have Cs(3)-Cs(3) distances of 2.71(1) Å or 3.85(1) or both. The shorter distance is impossibly short, even less than the sum of the cationic radii of two Cs$^+$ ions, 3.34 Å, and cannot be tolerated. To avoid it, three Cs(3)'s must form an equilateral triangle with 3.85 Å distances (see Figures 4 and 5). These distances are still quite short, as compared to the bond legth in Cs metal, 5.31 Å, for example. This indicates that at least some of the electrons of the sorbed Cs atoms are at least partly delocalized over these three Cs(3) species. Similary short intercesium distances (*ca.* 3.89(2) Å) were found in the crystal structures of zeolite X treated with Cs vapor.[33]

All eight threefold-axis sites in the large cavity are occupied by Cs$^+$ ions at Cs(2), so Cs(2) and Cs(3) must interact. Three of the eight Cs$^+$ ions at Cs(2) must associte with the Cs(3) triangles to allow further electron delocalization. When only two Cs(3)'s are present in the sodalite unit, two of the eight Cs$^+$ ions at Cs(2) must associate with them. The sum of the occupancies of Cs(2) and Cs(3) is ten (in the case of two Cs species at Cs(3) or eleven (when there are three Cs species at Cs(3)). Of the ten or eleven Cs species, nine may be counted as Cs$^+$ ions (to balance framework charge) and one or two as Cs^0 atoms. This indicates that the clusters (Cs$_4$)$^{3+}$ (linear, see Figures 3 and 6) and (Cs$_6$)$^{4+}$ (a trigonal three legged stool, see Figures 4 and 5), and/or other such cationic clusters, have formed.

In crystal 2, the fractional occupancies observed at Cs(2) and Cs(3) indicate the presence of two types of "unit cells" with respect to the cations. About 60% of the unit cells may have eight Cs$^+$ ions at Cs(2) and two Cs$^+$ ions at Cs(3) and the remaining 40% would have seven Cs$^+$ ions at Cs(2) and three at Cs(3). All unit cells would have three Cs$^+$ ions at Cs(1). By the argument presented in the previous paragraph, (Cs$_4$)$^{3+}$ and (Cs$_6$)$^{4+}$ clusters (and perhaps (Cs$_5$)$^{4+}$) may exist. Some degree of arbitrainess is used in selecting these stoichiometries.

The sodalite unit with two Cs(3)'s may have Cs(3)-Cs(3) distances of *ca.* 4.70 Å, which are very long compared to the corresponding distances in linear (Cs$_4$)$^{3+}$, 3.88 to 4.26 Å.[12,13] The intercesium distances for the corresponding linear (Cs$_4$)$^{3+}$ cluster in the present work are *ca.* 3.65 Å, 4.70 Å, and 3.65 Å for Cs(2)-Cs(3), Cs(3)-Cs(3), and Cs(3)-Cs(2), respectively.

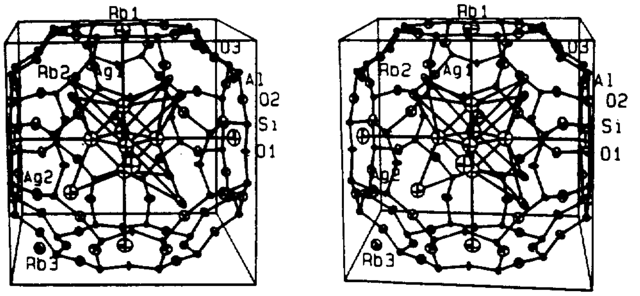

Figure 7. A stereoview of the large cavity of the dehydrated $Ag_{5.6}K_{6.4}$-A treated with Rb vapor. Ellipsoids of 20% probability are used.

This indicates that the electron density of $(Cs_4)^{3+}$ cluster is localized toward the Cs^+ ions at Cs(2), which also coordinate to and stabilize the hexasilver cluster. Some of Cs^+ ions at Cs(2) also stabilize $(Cs_3)^+$, which is larger than $(Cs_2)^+$. These ions at Cs(2) are less likely to interact with a hexasilver cluster. Then of the 15 or 16 Cs^+ ions at Cs(2) (considering two unit cells) for crystals 2 and 3, respectively, only 12 (12/15=0.80, corresponding to 80% of Cs^+ ions at Cs(2) or 80% of large cavity) or 13 Cs^+ ions (13/16=0.81, 81%) can participate in stabilizing hexasilver clusters. Similarly long Rb(3) to Rb(3) distances, *ca.* 4.60 Å, were observed in $(Rb_4)^{3+}$ clusters in previous studies of the crystal structures of $Ag_{12-2x}Ca_x$-A reacted with Rb(g).[32]

Crystal 4, approximate composition $Ag_{3.4}Rb_{11.0}$-A. In this reaction of $Ag_{5.6}K_{6.4}$-A treated with Rb(g), K^+ and Ag^+ ions were also reduced by Rb vapor. Rb^+ ions are found at three different crystallographic sites: Rb(1) at 8-ring centers, Rb(2) on threefold axes opposite the 6-rings deep in the large cavity, and Rb(3) on threefold axes in the sodalite unit. No excess Rb atom sorption is seen. However, Ag atoms are found in the large cavity.

The numbers of Rb^+ ions at Rb(1), Rb(2), and Rb(3) per unit cell are *ca.* 3.0, 5.7, and 2.3, respectively. Three Rb^+ ions at Rb(1) fill at the centers of 8-rings and each Rb(1) ion is *ca.* 3.37(3) Å from O(1) oxygens and *ca.* 3.65(1) Å from O(2)'s. These distances are substantially longer than the sum of the ionic radii of O^{2-} and Rb^+, 2.79 Å. Rb^+ ions have been observed at this site in all previous studies of Rb^+ in zeolite A, with similar long contact distances.[16] Each ion at Rb(2) is *ca.* 2.91(1) Å from the three O(3) oxygens of its 6-ring and *ca.* 1.66 Å from the (111) plane at O(3). Rb^+ ions at Rb(3) are inside the sodalite unit, *ca.* 2.88(2) Å from three O(3) oxygens and *ca.* 1.62 Å from its (111) plane (see Table 3).

The fractional occupancies observed at Rb(2) and Rb(3) indicate the existence of at least two type of unit cells with regard to the 6-rings. For example, about 70% of unit cells may have 6 Rb^+ ions at Rb(2) and 2 Rb^+ ions at Rb(3). The remaining 30% of unit cells would have 5 Rb^+ ions at Rb(2) and 3 Rb^+ ions at Rb(3).

Ag species are found at two crystallographic sites: 2.4 Ag atoms are found at Ag(1), deep within the large cavity. One Ag^+ ion at Ag(2) is found opposite a 4-ring in the large cavity. The distance between Ag(1) and O(1), *ca.* 5.41(3) Å, is very much longer than the sum of the ionic radii, 2.58 Å. This indicates that the species at Ag(1) must be Ag^0 and not Ag^+. Also, the shortest distance between Ag(1) and Ag(1), *ca.* 2.68(3) Å, is similar to the corresponding distance in crystals 2 and 3. These Ag species may form hexasilver clusters at the center of about 40% of large cavities (see Figure 7).

The distances from Ag(1) to Rb(1) and Rb(2) are *ca.* 4.23 and 4.12 Å, respectively. These are almost the same as the sum of the van der Waals radius of Ag^0 and the ionic radius of Rb^+, 4.14 Å. Such a sum was found to describe Ag^+ and Ag^0 contacts quite accurately.[1,2] The hexasilver cluster may be stabilized by the coordination interaction with Rb^+ ions at Rb(1) and Rb(2). The relatively large thermal ellipsoids of Ag(2) indicate that the hexasilver cluster is loosely held at its positions.

In this structure, the Ag^+ ion at Ag(2) is distributed over a 12-fold equipoint in the large cavity on a twofold axis opposite a 4-ring (see Figure 5). This ion is rather far from framework oxygens Ag(2)-O(1)=2.95(6) Å and Ag(2)-O(3)=2.91(4) Å probably because of an interaction with an Rb^+ ion at Rb(3). The distance between Ag(1) and Ag(2) is 3.35 Å which is almost the same as that between Ag^+ and Ag^0 in previous studies.[1,2] Such Ag^+ positions were also found in the structures of Ag, Ca-A treated with Rb vapor.[32]

In the structures, Cs and/or Rb(g) reacted with dehydrated zeolite A to perform a solvent-free redox ion exchange. The hexasilver cluster in the large cavity is stabilized by coordination to Cs^+ or Rb^+ ions in these structures. Excess Cs atoms were sorbed to form cluster such as $(Cs_4)^{3+}$ or $(Cs_6)^{4+}$. In contrast, Rb clusters are not found in the crystal structure of $Ag_{5.6}K_{6.4}$-A reacted with Rb(g). It appears that zeolites exposed to Cs metal vapor readily absorb extra metal atoms into their cavities to form Cs clusters.

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Laser Induced Impedance Changes in Hollow Cathode Lamps

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Laser induced impedance changes in hollow cathode lamps containing sputtered metal atoms have been employed to measure the spectroscopic properties of metal. This technique, known as optogalvanic spectroscopy, has been shown to be a powerful and inexpensive technique for the investigation of atomic and molecular species. Characteristic optogalvanic signals from hollow chthode lamps (HCL) made of different metal species and induced with a pulsed dye laser were observed, and the dependence of the optogalvanic signal on the discharge current and wavelength of laser was measured. Based on the results obtained, the mechanisms involved in evoking the optogalvanic signals were consisted of single-photon absorption, multi-photon absorption, and photoionization. Moreover the current dependence of the optogalvanic signal indicates that the optogalvanic technique could be one of the most sensitive optical methods of detecting atomic species.

Introduction

It is well known that the electric properties of a glow discharge change when it is illuminated with radiation that is resonant to the transitions of atoms contained in the discharge. This perturbation which is called the optogalvanic effect (OGE) is observed as changes in the electric conductivity of the discharge. The main advantage of applying OGE as an analytical tool comes from its simplicity and ease of use. The changes due to OGE can be converted readily into measurable electrical signal, thus, no other complicated optics are required.

The OG effect was first observed by Penning.[1,2] Others reported the same effect in different discharges,[3,4] but the practical application of the OGE began with the introduction of the laser. This effect in relation to the laser was first discovered in a gas discharge laser. When a gas discharge laser was operated, changes were observed in the discharge current as the laser came over the threshold.[5-9] The actual development of the OGE as a useful spectroscopic tool started with the work of Green *et al.* who used a tunable dye laser and obtained highly sensitive spectra of the species present in the discharge.[10] They have shown how this technique could be studied with commercial hollow cathode lamps. Zalewski *et al.* also used commercial hollow cathode lamps.[11] Wide-ranging applications of the OGE followed, such as the detection of low concentrations or trace element analysis, isotopic analysis of lanthanides, OG spectroscopy with a pulse

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