

## Crystal Structures of Bromine Sorption Complexes of Ca<sup>2+</sup>-Exchanged Zeolite A

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The structures of dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A ( $a=12.243(1)$  Å) and of its bromine sorption complex ( $a=12.214(1)$  Å) have been determined by single crystal x-ray diffraction techniques in the cubic space group  $Pm\bar{3}m$  at 21(1) °C. Both crystals were dehydrated at 360 °C and  $2 \times 10^{-6}$  Torr for 2 days and one crystal was treated with 180 Torr of bromine vapor at 24 °C for 1 h. The structures were refined to final error indices,  $R_1=0.066$  and  $R_2=0.078$  with 192 reflections and  $R_1=0.109$  and  $R_2=0.093$  with 100 reflections, respectively, for which  $I > 3\sigma(I)$ . In these structures, four Ca<sup>2+</sup> and four Na<sup>+</sup> ions are located on two different threefold axes associated with 6-ring oxygens, respectively. In Ca<sub>4</sub>Na<sub>4</sub>-A·6Br<sub>2</sub>, four Ca<sup>2+</sup> ions are recessed 0.28(1) Å into the large cavity and four Na<sup>+</sup> ions extend 0.63(1) Å into the sodalite unit. A total of six dibromine molecules are sorbed per unit cell. Each Br<sub>2</sub> molecule approaches a framework oxide ion axially with O(1)-Br(1)=3.27(2) Å, Br(1)-Br(2)=2.66(6) Å and O(1)-Br(1)-Br(2)=172(1)°, indicating a charge-transfer interaction.

### Introduction

Cation-modified type A zeolites are of commercial interest for the adsorptive separation process of several gas mixtures. Calcium exchanged zeolites especially are used industrially for drying and purifying of natural gas. Zeolites with calcium contents of 60-80% are mainly employed, where either the pore opening of the eight-rings, or the interaction between the cations and polar molecules is of primary importance.

In the crystal structure of an iodine sorption complex of Ca<sub>4</sub>Na<sub>4</sub>-A<sup>1,2</sup> and that of a bromine sorption complex of dehydrated fully Ag<sup>+</sup>-exchanged zeolite A,<sup>3</sup> the halogen molecules interact with oxide ions of the zeolite framework. In these structures, the Br<sub>2</sub> and I<sub>2</sub> molecules act as Lewis acids with respect to framework oxide ion lone pairs. Linear X-X-O sequences, with the X<sub>2</sub> bond lengthened by complexation,<sup>4,5</sup> were found in these charge-transfer complexes (O-I-I=178° and O-Br-Br=174(4)°). On the other hand, in the structure of a bromine sorption complex of Na<sub>12</sub>-A,<sup>6</sup> about six bromine molecules per unit cell were found to interact neither with the anionic framework nor with the 8 of the 12 Na<sup>+</sup> ions per unit cell which were located.

Several structures of Cl<sub>2</sub> and Br<sub>2</sub> sorption complexes of Ag<sup>+</sup>,<sup>7</sup> Eu(II),<sup>8</sup> and Co(II)-exchanged<sup>9</sup> zeolite A have been determined. In the structure of a chlorine sorption complex of vacuum-dehydrated Eu(II)-exchanged zeolite A, dichlorine has oxidized Eu(II) to Eu(IV).<sup>8</sup> Chlorine gas also oxidizes hexasilver to AgCl as observed in the structure of a chlorine sorption complex of dehydrated, fully Ag<sup>+</sup>-exchanged zeolite A.<sup>7</sup> An additional six molecules per unit cell of dichlorine are sorbed which form charge transfer complexes with framework oxide ions (O-Cl-Cl=166(2)°). In the crystal structure of a Cl<sub>2</sub> sorption complex of Co<sub>4</sub>Na<sub>4</sub>-A,<sup>9</sup> four chlorine molecules act as ligands to coordinate, each to one Co(II) ion, in a bent manner.

According to recent reports, zeolite minerals have found increasing application in the field of pollution abatement.<sup>10</sup> For example, natural zeolites have been used to remove car-

bon dioxide from contaminated and sour natural gas.<sup>11</sup> Perhaps Ca<sub>4</sub>Na<sub>4</sub>-A could be used to remove Br<sub>2</sub> from industrial environments.

This work was initiated to investigate the cation positions in the crystal structure of the dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A, to investigate bromine sorption by Ca<sub>4</sub>Na<sub>4</sub>-A and to determine the positions of sorbed bromine molecules.

### Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method.<sup>12</sup> Each of two single crystals about 85 μm on edge was selected and lodged in a fine quartz capillary. Ca<sub>4</sub>Na<sub>4</sub>Si<sub>12</sub>Al<sub>12</sub>O<sub>48</sub>·xH<sub>2</sub>O were prepared by flow methods using exchange solutions in which molar ratios of Ca(NO<sub>3</sub>)<sub>2</sub> and NaOH were 100 : 1, with a total concentration 0.05 M. Ion exchange was accomplished by allowing the solution to flow past each crystal at a velocity of approximately 1.2 cm/sec for 3 days at 21(1) °C.

Each crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (*ca.* 25 °C/h) to 360 °C at a constant pressure of  $2 \times 10^{-6}$  Torr. Finally, the system was maintained at the state for 48 h. After cooling to room temperature, one crystal (the first crystal), still under vacuum, was sealed in its capillary by torch. Both crystals were colorless. To prepare the bromine complex, the dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A crystal was treated with 180 Torr zeolitically dried bromine vapor at 24 °C for 1 h. The colorless dehydrated crystal immediately become dark red. After about 1 h, the crystal, still in its bromine atmosphere, was sealed in its capillary by torch.

### X-ray Data Collection

The cubic space group  $Pm\bar{3}m$  (no systematic absences) was used instead of  $Fm\bar{3}c$  throughout this work due to reasons discussed previously.<sup>13,14</sup> Diffraction data were collected

with an automated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a pulse-height analyzer and a graphite monochromator, using Mo K $\alpha$  radiation (K $\alpha_1$ ,  $\lambda=0.70930$  Å, K $\alpha_2$ ,  $\lambda=0.71359$  Å). The unit cell constants at 21(1) °C determined by least squares refinement of 25 intense reflections for which  $18^\circ < 2\theta < 25^\circ$  are  $a=12.243(1)$  Å for Ca $_4$ Na $_4$ -A and  $a=12.214(1)$  Å for the bromine sorption complex of Ca $_4$ Na $_4$ -A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space ( $hkl$ ,  $0 \leq h \leq k \leq l$  and  $lhk$ ,  $0 \leq l \leq h \leq k$ ) were examined. The intensities were measured using  $\omega$ - $2\theta$  scan technique over a scan width of  $(0.80 + 0.344 \tan \theta)^\circ$  in  $\omega$ . The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between  $0.25^\circ$  and  $0.32^\circ$  deg min $^{-1}$  in  $\omega$ . The intensities of three reflections in diverse regions of reciprocal space were recorded after every three hours to monitor crystal and x-ray source stability. Only small and 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  $2\theta < 70^\circ$  were recorded. Only those of which  $I > 3\sigma(I)$  were used for structure solution and refinement. These amounted to 192 of the 872 reflections for the first crystal, and 100 of the 867 reflections for crystal 2.

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.<sup>15</sup>

For the first crystal,  $\mu R=0.031$ ,  $\rho_{cal}=1.534$  g/cm $^3$  and  $F(000)=830$ ; for the second the corresponding values are 0.331, 2.403 g/cm $^3$  and 1250. The absorption correction was judged to be negligible for both crystals and was not applied.<sup>16</sup>

## Structure Determination

**Dehydrated Ca $_4$ Na $_4$ -A.** Full-matrix least-squares refinement was initiated by using the atomic parameters of the framework atoms [(Si,Al), O(1), O(2), and O(3)] from the structure of dehydrated Co $_4$ Na $_4$ -A.<sup>17</sup> Anisotropic refinement of the framework atoms converged to an  $R_1$  index,  $(\sum |F_o - |F_c||)/\sum F_o$  of 0.381 and a weighted  $R_2$  index,  $(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$  of 0.432.

The initial difference Fourier function revealed one large peak at (0.193, 0.193, 0.193) of height of  $3.89(20)$  eÅ $^{-3}$ . Inclusion of this peak as Ca(1) lowered the error indices of  $R_1=0.168$  and  $R_2=0.171$  (see Table 1).

A difference Fourier function revealed a peak at (0.166, 0.166, 0.166) with a height of  $2.95(19)$  eÅ $^{-3}$ . Simultaneous positional, thermal, and occupancy refinement including this positions as Na(1) converged to  $R_1=0.056$  and  $R_2=0.067$ .

It is not so difficult to distinguish Ca $^{2+}$  from Na $^+$  ions for several reasons. First, the atomic scattering factor are different,  $18 e^-$  for Ca $^{2+}$  vs.  $10 e^-$  for Na $^+$ . Secondly, the ions at Ca(1) and Na(1) are associated with 6-rings and lie on threefold axes. If Ca $^{2+}$  ions at Ca(1) were actually Na $^+$  ions, the sum of Na $^+$  ions on the threefold axes were about

**Table 1.** Positional, Thermal, and Occupancy Parameters Crystal 1. Dehydrated Ca $_4$ Na $_4$ -A

Atom	Wyc. Pos.	x	y	z	$^b\beta_{11}$ B $_{iso}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy	
											varied	fixed
(Si,Al)	24(k)	0	1829(4)	3701(3)	39(2)	27(2)	18(2)	0	0	10(5)		24.0 <sup>d</sup>
O(1)	12(h)	0	2130(10)	5000	60(10)	70(10)	40(10)	0	0	0		12.0
O(2)	12(i)	0	2887(8)	2887(8)	130(20)	42(7)	42(7)	0	0	40(20)		12.0
O(3)	24(m)	1104(5)	1104(5)	3349(7)	65(5)	65(5)	44(8)	40(20)	-10(10)	-10(10)		24.0
Ca(1)	8(g)	2088(7)	2088(7)	2088(7)	72(5)	72(5)	72(5)	60(10)	60(10)	60(10)	3.98(7)	4.0
Na(1)	8(g)	1630(20)	1630(20)	1630(20)	10(1) <sup>e</sup>						3.87(8)	4.0

**Crystal 2.** Bromine Sorption Complexes of Dehydrated Ca $_4$ Na $_4$ -A

Atom	Wyc. Pos.	x	y	z	$^b\beta_{11}$ B $_{iso}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	Occupancy	
											varied	fixed
(Si,Al)	24(k)	0	1820(10)	3727(9)	26(6)	34(7)	31(7)	0	0	-20(20)		24.0 <sup>d</sup>
O(1)	12(h)	0	2120(30)	5000	270(50)	100(40)	160(40)	0	0	0		12.0
O(2)	12(i)	0	2830(20)	2830(20)	150(40)	130(20)	130(20)	0	0	110(50)		12.0
O(3)	24(m)	1070(20)	1070(20)	3350(20)	200(10)	200(10)	190(30)	210(40)	80(40)	80(40)		24.0
Ca(1)	8(g)	1960(20)	1960(20)	1960(20)	140(20)	140(20)	140(20)	120(50)	120(50)	120(50)	3.82(8)	4.0
Na(1)	8(g)	1530(30)	1530(30)	1530(30)	100(30)	100(30)	100(30)	80(60)	80(60)	80(60)	3.76(7)	4.0
Br(1)	12(l)	1250(30)	4490(40)	5000	490(60)	1300(200)	210(40)	-400(200)	0	0	5.78(14)	6.0
Br(2)	24(l)	2520(30)	3740(50)	5000	400(50)	670(80)	1500(200)	-700(100)	0	0	6.23(13)	6.0

<sup>a</sup>Positional and anisotropic thermal parameters are given  $\times 10^4$ . Numbers in parentheses are the esd's in the units of the least significant digit given for the corresponding parameter. <sup>b</sup>The anisotropic temperature factor =  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ . <sup>c</sup>Occupancy factors are given as the number of atoms or ions per unit cell. <sup>d</sup>Occupancy for (Si)=12; occupancy for (Al)=12. <sup>e</sup>Isotropic thermal parameter in unit Å $^2$ .

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

	Ca <sub>4</sub> Na <sub>4</sub> -A	Ca <sub>4</sub> Na <sub>4</sub> -A·6Br <sub>2</sub>
(Si,Al)-O(1)	1.632(5)	1.60(1)
(Si,Al)-O(2)	1.634(7)	1.65(2)
(Si,Al)-O(3)	1.674(5)	1.66(1)
Ca(1)-O(3)	2.30(1)	2.30(2)
Na(1)-O(3)	2.30(2)	2.37(2)
Br(2)-Br(1)		2.66(6)
Br(1)-O(1)		3.27(3)
Br(1)-O(2)		3.68(1)
O(1)-(Si,Al)-O(2)	114.8(7)	119(1)
O(1)-(Si,Al)-O(3)	111.6(4)	110(1)
O(2)-(Si,Al)-O(3)	105.3(3)	103.3(8)
O(3)-(Si,Al)-O(3)	107.8(3)	104(1)
(Si,Al)-O(1)-(Si,Al)	154(2)	153(2)
(Si,Al)-O(2)-(Si,Al)	165.2(5)	173(1)
(Si,Al)-O(3)-(Si,Al)	142.3(5)	142(1)
O(3)-Ca(1)-O(3)	115.5(2)	118.6(6)
O(3)-Na(1)-O(3)	115.7(6)	113(1)
O(1)-Br(1)-Br(2)		172(1)
O(2)-Br(1)-Br(2)		157.6(8)

Numbers in parentheses are estimated standard deviations in the least significant digit given for the corresponding value.

twelve. However, the maximum number of ions per unit cell at these positions cannot sum to more than eight; otherwise unacceptably close intercationic distance would occur. Finally, the approach distances between those cations and zeolite oxides in dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A have been determined by the powder diffraction methods and indicative.<sup>1</sup>

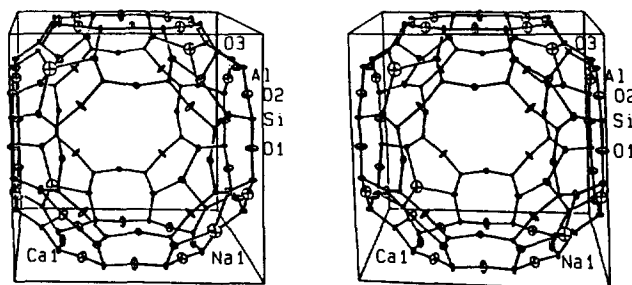
The occupancy numbers of Ca<sup>2+</sup> and Na<sup>+</sup> ions per unit cell were refined to Ca(1)=3.98(7), and Na(1)=3.87(8). These were fixed at Ca(1)=4.0, Na(1)=4.0, respectively because the cationic charge should not be exceeded +12 per *Pm3m* unit cell. Anisotropic refinement of the framework atoms and cations at Ca(1) and Na(1) converged to *R*<sub>1</sub>=0.066 and *R*<sub>2</sub>=0.078 (see Table 1).

In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.1% of their corresponding standard deviations. The final difference function was featureless except for a peak at (0.0, 0.0, 0.0) of height 1.7(6) eÅ<sup>-3</sup>. This peak was not within bonding distance of any other atom, and was not considered further.

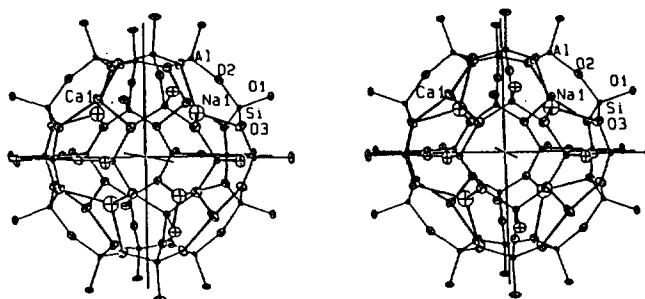
**Bromine sorption complexes of the dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A.** Full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms from the previous crystal of Ca<sub>4</sub>Na<sub>4</sub>-A.<sup>14</sup> Anisotropic refinement of the framework atoms converged to *R*<sub>1</sub>=0.49 and *R*<sub>2</sub>=0.65, respectively.

The initial difference Fourier function revealed one large peak at (0.193, 0.193, 0.193) of height 3.88(28) eÅ<sup>-3</sup>. Inclusion of this peak as Ca(1) lowered the error indices to *R*<sub>1</sub>=0.315 and *R*<sub>2</sub>=0.369 (see Table 1).

A subsequent difference Fourier synthesis revealed two large peaks at (0.138, 0.416, 0.5) and (0.277, 0.359, 0.5) with a peak height of 1.89(19) eÅ<sup>-3</sup> and 2.04(18) eÅ<sup>-3</sup>, respectively. These peaks were stable in least-squares refinement.



**Figure 1.** A stereoview of large cavity of dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A. Four Ca<sup>2+</sup> ions at Ca(1) and four Na<sup>+</sup> ions at Na(1) are shown. Ellipsoids of 20% probability are shown.



**Figure 2.** A stereoview of the sodalite unit of dehydrated Ca<sub>4</sub>Na<sub>4</sub>-A. Four Ca<sup>2+</sup> ions at Ca(1) and four Na<sup>+</sup> ions at Na(1) are shown. Ellipsoids of 20% probability are used.

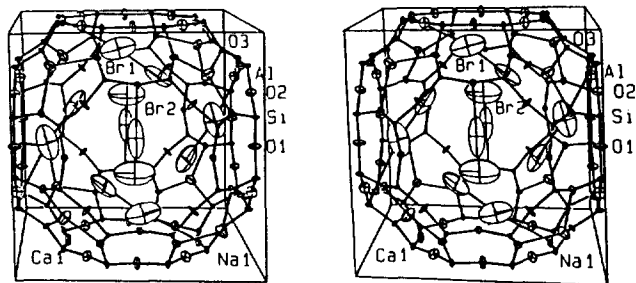
Including these peaks as Br(1) and Br(2) lowered the error indices to *R*<sub>1</sub>=0.148 and *R*<sub>2</sub>=0.136 (see Table 1).

A difference Fourier function revealed a peak at (0.166, 0.166, 0.166) with a height of 2.38(25) eÅ<sup>-3</sup>. Simultaneous positional, thermal, and occupancy refinement including this position as Na(1) converged to *R*<sub>1</sub>=0.097 and *R*<sub>2</sub>=0.086. The Ca(1) and Na(1) occupancies were reset and fixed as shown in Table 1.

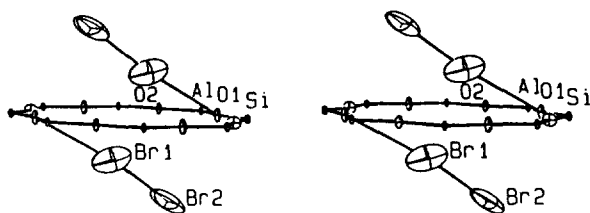
The occupancy numbers of bromines at Br(1) and Br(2) were refined to Br(1)=5.78(14) and Br(2)=6.24(13), respectively. These were reset and fixed at Br=6.0, the maximum number of atoms at each of these positions for packing reasons. It is furthermore reasonable that these two occupancies should be equal because the distance involved indicates that these positions represent dibromine molecules (see Table 1).

The final error indices were *R*<sub>1</sub>=0.109 and *R*<sub>2</sub>=0.093. The final difference function was featureless except 1.98(64) eÅ<sup>-3</sup> at (0.0, 0.0, 0.0). This peak was not refined at the least-squares refinement.

For all structures, the full-matrix least-squares program used minimized  $\sum w(F_o - |F_c|)^2$ ; the weight (*w*) of an observation was the reciprocal square of  $\sigma(F_o)$ , its standard deviation. Atomic scattering factors<sup>18,19</sup> for Ca<sup>2+</sup>, Na<sup>+</sup>, Br<sup>0</sup>, O<sup>-</sup>, and (Si, Al)<sup>1.75+</sup> were used. The function describing (Si, Al)<sup>1.75+</sup> is the mean of the Si<sup>0</sup>, Si<sup>4+</sup>, Al<sup>0</sup>, and Al<sup>3+</sup> functions. All scattering factors were modified to account for the anomalous dispersion correction.<sup>20</sup> The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.



**Figure 3.** The unit cell of bromine sorption complexes of the dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$  is stereoview. Four  $\text{Ca}^{2+}$  ions at Ca(1), four  $\text{Na}^+$  ions at Na(1) and 6 dibromine molecules are shown. Ellipsoids of 20% probability are used.



**Figure 4.** Each 8-oxygen ring in the structure participates in a charge transfer interaction with two dibromines as shown. Ellipsoids of 20% probability are used.

## Discussion

In the crystal structure of vacuum dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$ , all  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions are found on two distinguished three fold axis (see Table 1 and Figure 1). About 4.0  $\text{Ca}^{2+}$  ions at Ca(1) extends 0.50 Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.30(1) Å in a slightly distorted trigonal planar arrangement. About 4.0  $\text{Na}^+$  ions at Na(1) are recessed 0.48 Å into the sodalite unit from the O(3) planes of the 6-ring. Each of these  $\text{Na}^+$  ions at Na(1) is coordinated to three O(3) framework oxygens at 2.30(2) Å. Although only average O(3) positions have been found in the present structural studies, the (Si, Al)-O(3) distances (also averages) in both structures are significantly longer than the (Si, Al)-O(1) and (Si, Al)-O(2) distances. All eight of  $\text{Ca}^{2+}$  and  $\text{Na}^+$  ions are associated with O(3) oxygens and consequently the (Si, Al)-O(3) bond has been weakened and lengthened. This effect has also been observed and discussed previously.<sup>21</sup>

In the bromine sorption complex of dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$ , 4  $\text{Ca}^{2+}$  ions at Ca(1) and 4  $\text{Na}^+$  ions at Na(1) occupy 6-ring sites on the threefold axes of unit cell (see Table 1 and Figure 3). About 4.0  $\text{Ca}^{2+}$  ions at Ca(1) extends 0.28 Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.30(2) Å in a slightly distorted trigonal planar arrangement. About 4.0  $\text{Na}^+$  ions at Na(1) are recessed 0.63 Å into the sodalite unit from the O(3) planes of the 6-ring. Each of these  $\text{Na}^+$  ions at Na(1) is coordinated two three O(3) framework oxygens at 2.37(2) Å. The length of the Ca(1)-O(3) bond is 2.30(2) Å. For comparison, the sum the conventional ionic radii of  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  is 2.31 Å.<sup>22</sup> The O(3)-Ca(1)-O(3) bond angles for both

**Table 3.** Deviations of Atoms (Å) from (111) Plane at O(3)

	$\text{Ca}_4\text{Na}_4\text{-A}$	$\text{Ca}_4\text{Na}_4\text{-A}\cdot 6\text{Br}_2$
O(2)	0.15(1)	0.12(1)
Ca(1)	0.50(1)	0.28(1)
Na(1)	-0.48(1)	-0.63(1)

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

structures are close to near trigonal planers; 115.5(2)° in vacuum dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$  and 118.6(4)° in its bromine complex.

In this work, bromine atoms have been found at two different 24-fold positions. These are interpreted to give two 24-fold molecular positions which are occupied statistically by six dibromine molecules. Six molecules is the maximum number which can be accommodated at these sites; otherwise, unreasonably short Br-Br distances, corresponding to overlapping molecules, would result. For the 6.0 Br(1)-Br(2) molecules, the closest approach of Br(1) position to the framework is to O(1). The dibromine molecule acts as a Lewis acid with respect to the framework oxide ion at O(1) which has lone pair electrons. Furthermore, the O(1)-Br(1)-Br(2) angle 172(1)° is close to linear. The bonding can be understood in terms of charge transfer complexation; the electronegative oxide ion at O(1) donates electron pair density axially to the vacant  $4p\sigma^*$  antibonding molecule. Accordingly, the Br-Br bond order is reduced and the Br-Br bond is 2.66(6) Å. This bond length is reasonably longer than that in free dibromine, 2.29 Å.<sup>23</sup>

The Br(1)-O(1) approach distance, 3.27(3) Å, is less than the nonbonded approach distance 3.35 Å,<sup>24</sup> calculated from the sum of the appropriate nonbonded van der Waals radii. These Br(1)-O(1) distances indicate the existence of charge transfer complex between these dibromine molecules and framework oxide ions at O(1). However, the sorption of bromine has little effect on the framework structure of zeolite compared with that of dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$ .

Recently, the crystal structure of a bromine sorption complex of partially cobalt(II)-exchanged zeolite A has been determined.<sup>25</sup> In this structure, a redox reaction has apparently occurred between Co(II) and  $\text{Br}_2$  to yield Co(III) and  $\text{Br}_3^-$  ions. The 4  $\text{Na}^+$  and 4  $\text{Co}^{3+}$  ions per unit cell occupy 6-ring sites on 3-fold axes. Each  $\text{Na}^+$  ion is recessed *ca.* 0.33 Å into the sodalite unit, whereas each  $\text{Co}^{3+}$  ion is *ca.* 0.54 Å on the large-cavity side of the plane of its 3 coordinating oxygens. Four quite asymmetric  $\text{Br}_3^-$  ions, each bridges between a  $\text{Co}^{3+}$  ion and an 8-ring framework oxygen (Co-Br-Br)=116°, (Br-Br-Br)=138°, and Br-Br-O=177°; the corresponding Co-Br-Br-Br-O distances are 2.59(1), 2.28(1), 2.64(3), and 3.40(2) Å, respectively). The near-linear Br-Br-O angle is indicative of a charge-transfer interaction. Two other bromine molecules similarly form charge-transfer complexes with 8-ring oxygens. However, in the work, the closest approach distance of a bromine atom to  $\text{Ca}^{2+}$  ion is 4.04(1) Å (see Figure. 3 and 4). Therefore, dibromine molecule makes no significant approach to  $\text{Ca}^{2+}$  ions.

The present structure is very similar to the structure of a iodine sorption complex of dehydrated  $\text{Ca}_4\text{Na}_4\text{-A}$ .<sup>12</sup> In this

structure, all 8 cations are associated with 6-ring oxygens; 4  $\text{Ca}^{2+}$  ions are moved *ca.* 0.22 Å into the large cavity from the (111) plane of the O(3) oxygens, and 4  $\text{Na}^+$  ions are displaced *ca.* 0.58 Å into the sodalite unit from the (111) plane of the O(3). About 5.65 diiodine molecules are sorbed per unit cell each  $\text{I}_2$  molecule make close approaches in its axial direction to a framework oxygen atom and to an iodine atom in an adjacent molecules, with an I-O distance of 3.29 Å and I-I distance of 2.72, and I-I-O=178°. The structure also indicates that diiodine molecule forms charge transfer complexes with framework oxygen.

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## Free-Standing Langmuir-Blodgett Films of Maleic Acid-Vinyl Ether Copolymers across 1 $\mu\text{m}$ Pores

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A coverage of about 1  $\mu\text{m}$ -sized pores of a membrane filter by four monolayers of maleic acids copolymers and poly(allylamine) (PAA) was attained by Langmuir-Blodgett (LB) technique through a covalent cross-linking followed a polyon complexation at the air-water interface. The copolymers were prepared to have side chains of hydrocarbon tail, carboxyl, and/or oligoether in the repeat unit. The surface pressure-area isotherms showed that the monolayers on an aqueous PAA have more expanded area than on pure water. The monolayers were transferable on a calcium fluoride substrate and a fluorocarbon membrane filter as Y deposition type, and the resulting LB films were characterized by FT-IR spectroscopy and scanning electron microscopy. A polymer network produced through interchain amide formation was confirmed in as-deposited films. The films were heat-treated in order to complete the cross-linking. SEM observation of the heat-treated film on a porous membrane filter showed that the four layer film was sufficiently stable to cover the filter pore of about 1  $\mu\text{m}$ . Immersion of the film in water or in chloroform did not cause any change in its appearance on SEM and in FT-IR spectra.

### Introduction

Langmuir-Blodgett (LB) films transferred onto porous membrane substrates are of interest, because the surface-modified

composite films can produce new functionalities.<sup>1</sup> For example, selective permeations of gases or biomolecules through the molecularly-thin organized films may be useful for separation<sup>2</sup> and sensor<sup>3</sup> applications. For this purpose, the mecha-