

부분적으로 Co(II) 이온으로 치환한 제올라이트 A를 탈수한 후 메탄올을 흡착한 결정구조

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Crystal Structure of a Methanol Sorption Complex of Dehydrated Partially Cobalt(II)-Exchanged Zeolite A

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요 약. 부분적으로 Co^{2+} 이온으로 치환한 제올라이트 A를 탈수한 후 메탄올을 흡착한 결정구조 즉 $\text{Co}_4\text{Na}_4\text{Si}_{12}\text{Al}_2\text{O}_{48} \cdot 6.5\text{CH}_3\text{OH}$ ($a=12.169(1) \text{ \AA}$)를 입방공간군 $Pm\bar{3}m$ 를 사용하여 단결정 X-선 회절법으로 해석하고 정밀화하였다. $\text{Co}_4\text{Na}_4\text{-A}$ 제올라이트를 360°C 에서 2×10^{-6} torr 하에서 2일간 진공탈수한 후 $22(1)^\circ\text{C}$ 에서 약 104 torr의 메탄올 증기로 약 1시간 동안 흡착시켜 결정을 만들었다. Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$ 인 147개의 독립반사를 사용하여 최종오차인자를 $R_1=0.061$, $R_2=0.060$ 까지 정밀화시켰다. 단위세포당 4개의 Co^{2+} 이온과 1.5개의 Na^+ 이온은 6-링 산소와 결합하고 있었다. 4개의 Co^{2+} 이온은 O(3)의 (111) 평면에서 큰 동공쪽으로 약 0.44 \AA 들어가 위치하고 1.5개의 Na^+ 이온은 O(3)의 (111) 평면에서 소다라이트 동공 깊숙히 약 0.55 \AA 들어간 자리에 위치하고 있다. 2.5개의 Na^+ 이온은 8-링 평면에 위치한다. 단위세포당 약 6.5개의 메탄올 분자가 흡착되었다. 이들 메탄올 분자는 큰 동공내에 위치하고 있고 4개의 Co^{2+} 이온과 2.5개의 Na^+ 이온과 결합하고 있다. 4개의 메탄올의 산소는 6-링에 위치한 Co^{2+} 이온과 결합하고 나머지 2.5개의 메탄올의 산소는 8-링에 위치한 Na^+ 이온과 결합하고 있다.

ABSTRACT. The crystal structure of a methanol sorption complex of dehydrated partially Co(II)-exchanged zeolite A, $\text{Co}_4\text{Na}_4\text{-A} \cdot 6.5\text{CH}_3\text{OH}$ ($a=12.169(1) \text{ \AA}$), has been determined by single-crystal X-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at $21(1)^\circ\text{C}$. $\text{Co}_4\text{Na}_4\text{-A}$ was dehydrated at 360°C and 2×10^{-6} torr for 2 days, followed by exposure to about 104 torr of methanol vapor at $22(1)^\circ\text{C}$ for 1 hr. The structure was refined to final error indices, $R_1=0.061$ and $R_2=0.060$ with 147 reflections, for which $I > 3\sigma(I)$. In this structure, four Co^{2+} ions and 1.5 Na^+ ions per unit cell lie at 6-ring positions: the Na^+ ions are recessed 0.44 \AA into the sodalite unit and the Co(II) ions extend ca. 0.55 \AA into the large cavity. 2.5 Na^+ ions lie in an 8-oxygen ring plane. The 6.5 methanol molecules are sorbed per unit cell. The 6.5 methanol oxygens, all in the large cavity, associate with the 4 Co^{2+} ions and 2.5 Na^+ ions.

INTRODUCTION

Zeolites have been the subject of numerous investigations because of their importance in adsorption and catalysis.

Accordingly, a variety of reactions have been studied over transition metal exchanged zeolites. For example, the dehydrogena-

tion of alkanes¹, the conversion of alcohols to aldehydes and ketones², and the oxidation of n-hexane to carboxylic acids³⁻⁶ have been conducted over A- and X-type zeolites containing Cr(II), Mn(II), Fe(II), Co(II) or Ni(II) ions. Furthermore, the decomposition of ammonia (to N₂ and H₂)⁷, the preparation of CH₄ from CO and H₂⁸, and the production of CO₂ from CO and O₂⁹ have been carried out over bivalent transition metal ion-zeolite systems.

Interesting and characterizable transition metal complexes do form intrazeolitically. By means of reflectance spectroscopy, Klier and Ralek^{10,11} have studied complexes of Co(II) and Ni(II) with H₂O, NH₃, N₂O, and cyclopropane in A-type zeolite systems.

In the structure of dehydrated partially Co(II) exchanged zeolite A¹², it has been observed that upon dehydration (activation) the transition metal ions adopt positions close to the anionic zeolite framework where they achieve trigonal near-planar coordination. Subsequent treatment of the Co(II) with carbon monoxide yields four-coordinate Co(II) ions; that is, each Co(II) ion maintains its trigonal framework bonds and also binds one molecule of CO¹².

In recent years zeolite minerals have found increasing application in the field of pollution abatement¹³, and they are fast becoming standard components in the design and construction of such facilities. Both the ion-exchange and adsorption properties of zeolites can be utilized. For example, natural zeolites have been used to remove carbon dioxide from contaminated and sour natural gas¹⁴. Perhaps Co₄Na₄-A could be used to remove CH₃OH from industrial environments.

This work was initiated to locate the sorbed CH₃OH molecules within transition metal exchanged zeolite A, to determine shifts in cation and framework atomic positions, to observe cation-sorbate interactions, and perhaps to detect resultant changes in sorbed molecule geometry.

EXPERIMENTAL SECTION

Crystals of synthetic zeolite 4A were prepared

by a modification of Charnell's method¹⁵. Ion exchange with aqueous 0.1 M Co(NO₃)₂ was done by the static method¹². This yielded material whose approximate stoichiometry was Co₄Na₄Si₁₂-Al₁₂O₄₈·xH₂O per unit cell, subsequently to be referred to as Co₄Na₄-A, exclusive of water molecules. One of the largest single crystals from this experiment, about 85 μm along an edge, was selected for x-ray diffraction study. The crystal was placed in a finely drawn Pyrex capillary, attached to a vacuum system, and cautiously dehydrated by gradually incrementing its temperature (ca. 25 °C/h) to 360 °C at a constant pressure of 2×10⁻⁶ torr. Finally, the system was maintained at the state for 48 h. After cooling to room temperature, the crystal, now deep blue, still under vacuum, was sealed in its capillary by torch. To prepare the methanol sorption complex, the crystal was treated with ca. 104 torr of zeolitically dried methanol vapor at 22(1) °C for 1 h¹⁶. After about 1 h, the crystal, now black in color, still in its methanol 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 for reasons discussed previously^{17,18}. 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 MoK α radiation (*K*_{α1}, λ=0.70930 Å, *K*_{α2}, λ=0.71359 Å). The unit cell constant at 21(1) °C determined by least squares refinement of 25 intense reflections for which 18°<2θ<25° is *a*=12.169(1) Å at 24 °C.

Reflections from two intensity-equivalent regions of reciprocal space (*hkl*, 0≤*h*≤*k*≤*l* and *lkh*, 0≤*l*≤*h*≤*k*) were examined. The intensities were measured using the ω-2θ scan technique over a scan width of (0.80+0.344 tanθ)° in ω. The data were collected using the variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.25 and 0.30 deg min⁻¹ in ω. 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, random fluctuations of these check reflections were noted during the course of data collections. All unique reflections for which $2\theta < 60^\circ$ were examined by counter methods. Of the 576 pairs of reflections examined, only the 147 pairs for which $I > 3\sigma(I)$ were used in structure solution and refinement.

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 WEIGHT¹⁹.

An absorption correction ($\mu R = 0.06$ and $\rho_{\text{cal}} = 1.81 \text{ g/cm}^3$) was judged to be negligible and was not applied²⁰.

STRUCTURE DETERMINATION

Full-matrix least-squares refinement was initiated using the framework atom positions [(Si, Al), O(1), O(2) and O(3)] from the structure of dehydrated $\text{Co}_4\text{Na}_4\text{-A}^{12}$. Anisotropic refinement of the framework atoms converged to an unweighted R_1 index, $(\sum |F_o - F_c|) / \sum F_o$ of 0.28 and a weighted R_2 index, $(\sum w(F_o - F_c)^2 / \sum wF_o^2)^{1/2}$ of 0.33.

The initial difference Fourier function revealed

two large threefold axis peaks at (0.220, 0.220, 0.220) and (0.166, 0.166, 0.166) with heights of 8.4 (2) and 1.6(2) $\text{e}\text{\AA}^{-3}$, respectively. These two peaks were stable in least-squares refinement. Anisotropic refinement including these Co^{2+} ions at Co(1) and Na^+ ions at Na(1) positions converged to $R_1 = 0.099$ and $R_2 = 0.116$. Full-matrix least-squares refinement converged to the occupancies of Co(1) = 3.86(8) and Na(1) = 1.68(12).

A subsequent difference Fourier function revealed three peaks: (0.292, 0.332, 0.332), height 0.97 (15) $\text{e}\text{\AA}^{-3}$; (0.151, 0.443, 0.5), 1.10(18) $\text{e}\text{\AA}^{-3}$; and (0.277, 0.354, 0.446), 0.88(13) $\text{e}\text{\AA}^{-3}$. Inclusion of these peaks as O(4), O(5), and C(1) atoms lowered the error indices to $R_1 = 0.072$ and $R_2 = 0.077$ (see Table 1).

A difference Fourier function revealed a peak at (0.0, 0.44, 0.44) with a height of 1.08(25) $\text{e}\text{\AA}^{-3}$. Inclusion of this peak as Na(2) (see Table 1) lowered the error indices to $R_1 = 0.060$ and $R_2 = 0.056$. The occupancy number of Na^+ ions at Na(2) refined to 2.47(19) per unit cell.

The occupancy numbers at O(4), O(5), and C(1) refined to ca. 3.91(33), 2.60(22), and 8.01(34), respectively. The occupancies of Co(1) and O(4), Na(2) and O(5), and their interatomic distances, indicated that Co(1) associate with O(4) and Na(2) associated with O(5) so their occupancies were const-

Table 1. Positional, thermal, and occupancy parameters^a

Atom	Wyc. Pos.	x	y	z	β_{11}^b B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy ^c varied	fixed
(Si, Al)	24(k)	0	1823(4)	3689(3)	22(3)	17(3)	13(3)	0	0	-10(7)	24.0 ^d	
O(1)	12(h)	0	2130(10)	5000	70(20)	100(20)	10(10)	0	0	0	12.0	
O(2)	12(i)	0	2976(9)	2976(9)	20(8)	20(8)	26(5)	0	0	20(20)	12.0	
O(3)	24(m)	1126(6)	1126(6)	3313(9)	53(6)	53(6)	50(10)	40(20)	-30(10)	-30(10)	24.0	
Co(1)	8(g)	2116(5)	2116(5)	2116(5)	52(4)	52(4)	52(4)	21(9)	21(9)	21(9)	3.86(8)	4.0
Na(1)	8(g)	1640(30)	1640(30)	1640(30)	10(20)	10(20)	10(20)	0(40)	0(40)	0(40)	1.68(12)	1.5
Na(2)	12(i)	0	4390(50)	4390(50)	13(4) ^e						2.47(19)	2.5
O(4)	24(m)	3020(80)	3290(50)	3290(50)	8(3)						3.91(33)	4.0
O(5)	24(l)	1400(100)	4400(100)	5000	7(5)						2.60(22)	2.5
C(1)	48(n)	2720(90)	3610(90)	4500(100)	9(5)						8.01(34)	6.5

^aPositional 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. ^bThe anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^cOccupancy factors are given as the number of atoms or ions per unit cell. ^dOccupancy for (Si) = 12; occupancy for (Al) = 12. ^eIsotropic thermal parameters in units of \AA^2 .

rained to be equal at 4.0 and 2.5, respectively (see Table 1). The sum of occupancies of oxygens at O(4) and O(5) and the occupancy of carbons should be equal because the distances involved indicate that these positions represent methanol molecules (see Table 1 and 2). The final R values were $R_1 = 0.061$ and $R_2 = 0.060$. The final difference function was featureless except $1.8(7) \text{ e}\text{\AA}^{-3}$ at $(0.0, 0.0, 0.0)$. This peak was not refined at the least-squares refinement.

The quantity minimized in least squares was $w(F_o - |F_c|)^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F_o)$, the standard deviation of F_o . Atomic scattering factors^{21,22} for O^0 , C^0 (valence), Co^{2+} , Na^+ , O^- and $(Si, Al)^{1.75+}$ were used. The function describing $(Si, Al)^{1.75+}$ is the mean of the Si^0 , Si^{4+} , Al^0 and Al^{3+} functions. All scattering factors were modified to account for the

Table 2. Selected interatomic distances (\AA) and angles (deg)

(Si, Al)-O(1)	1.638(6)
(Si, Al)-O(2)	1.650(7)
(Si, Al)-O(3)	1.675(7)
Co(1)-O(3)	2.240(9)
Na(1)-O(3)	2.20(4)
Na(2)-O(1)	2.85(2)
Na(2)-O(2)	2.44(4)
Co(1)-O(4)	2.31(7)
Na(2)-O(5)	2.38(13)
O(4)-C(1)	1.53(9)
O(5)-C(1)	1.98(17)
O(1)-(Si, Al)-O(2)	108.6(8)
O(1)-(Si, Al)-O(3)	112.5(5)
O(2)-(Si, Al)-O(3)	106.7(4)
O(3)-(Si, Al)-O(3)	109.8(4)
(Si, Al)-O(1)-(Si, Al)	154(1)
(Si, Al)-O(2)-(Si, Al)	153.4(6)
(Si, Al)-O(3)-(Si, Al)	138.9(5)
O(3)-Co(1)-O(3)	114.2(3)
O(3)-Na(1)-O(3)	116.1(8)
Co(1)-O(4)-C(1)	110(3)
Na(2)-O(5)-C(1)	107(4)

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

anomalous dispersion correction²³. The final structural parameters and selected interatomic distances and angles are presented in Table 1 and 2, respectively.

DISCUSSION

In the structure of dehydrated partially Co_4Na_4 -A treated with methanol, 4.0 Co^{2+} ions at Co(1) lie on threefold axes of the unit cell and are recessed 0.55 \AA into large cavity from (111) planes at O(3) (see Table 3). Compared to dehydrated Co_4Na_4 -A¹², each of these ions has moved ca. 0.21 \AA further into the large cavity to coordinate to CH_3OH molecules. The length of the Co(1)-O(3) bond has increased from $2.077(18) \text{ \AA}$ in dehydrated Co_4Na_4 -A¹⁴ to $2.240(9) \text{ \AA}$ in this structure (see Table 2). Also, the O(3)-Co(1)-O(3) angle has decreased accordingly from the trigonal planar value of $117.4(12)^\circ$ to $114.2(3)^\circ$ after complexation.

The 1.5 Na^+ ions at Na(1) per unit cell are recessed 0.44 \AA into the sodalite unit from the O(3)

Table 3. Deviations of atoms (\AA) from (111) plane at O(3)

O(2)	0.27
Co(1)	0.55
Na(1)	-0.44
O(4)	2.84
C(1)	3.69

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

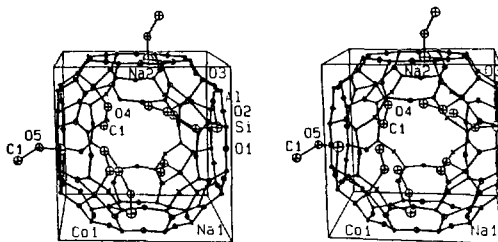


Fig. 1. One unit cell of this methanol complex of dehydrated Co_4Na_4 -A is shown in stereoview. Four Co^{2+} ions at Co(1), two Na^+ ions at Na(1), two Na^+ ions Na(2), and six methanol molecules per unit cell can be seen. About 50% of the unit cells have this arrangement. Ellipsoids of 20% probability are used.

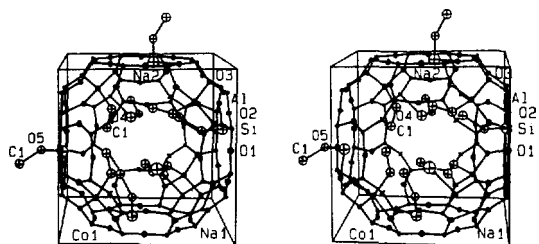


Fig. 2. One unit cell of this methanol complex of dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ is shown in stereoview. Four Co^{2+} ions at Co(1), one Na^+ ions at Na(1), three Na^+ ions Na(2), and seven methanol molecules per unit cell can be seen. About 50% of the unit cells have this arrangement. Ellipsoids of 20% probability are used.

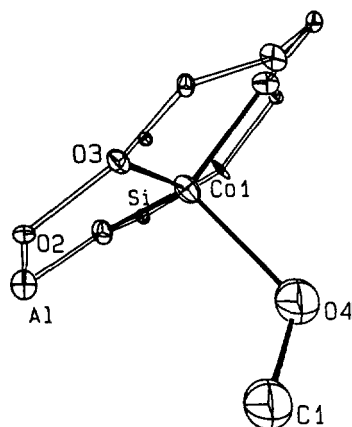


Fig. 3. A stereoview of one corner of the large cavity showing a CH_3OH molecules coordinated to a Co^{2+} ion at Co(1) and near to three framework oxygens. Ellipsoids of 20% probability are used.

plane of the 6-ring. Compared to dehydrated $\text{Co}_4\text{Na}_4\text{-A}$, each of these ions has moved ca. 0.12 \AA further into the sodalite cavity. The length of the Na(1)-O(3) bond has increased from $2.12(2) \text{ \AA}$ in dehydrated $\text{Co}_4\text{Na}_4\text{-A}$ to $2.20(4) \text{ \AA}$ in this structure (see Table 2). The angle subtended at Na(1), O(3)-Na(1)-O(3), is $116.1(8)^\circ$, indicating a near trigonal planar structure.

In dehydrated $\text{Co}_4\text{Na}_4\text{-A}$, four Co(II) and four Na^+ ions are located on the threefold axes close to the plane of the oxygen 6-rings. However, in the structure of the CH_3OH sorption complex of dehydrated $\text{Co}_4\text{Na}_4\text{-A}$, 2.5 Na^+ ion at Na(2) have relocated on the plane of 8-oxygen ring. In order

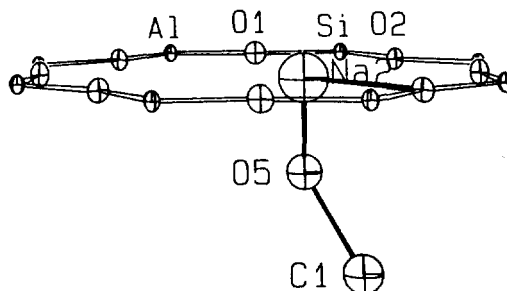


Fig. 4. A stereoview of one corner of the large cavity showing a CH_3OH molecules coordinated to a Na^+ ion at Na(2). Ellipsoids of 20% probability are used.

to make a favorable approach to framework oxygens, Na^+ ions at Na(2) lie off the center of its 8-ring.

The oxygen at O(4) and carbon at C(1) are located deep inside the large cavity (see Fig. 1 and 2). Each of the 4.0 Co^{2+} ions at Co(1) is complexed to one oxygen at O(4). The O(4)-C(1) distance is $1.53(9) \text{ \AA}$, about 0.10 \AA longer than the corresponding distance in CH_3OH (1.427 \AA)²⁴. The Co^{2+} -O(4) distance, $2.31(7) \text{ \AA}$, is longer than the sum of the ionic radius of Co^{2+} and the van der Waals radius of oxygen, $0.72 + 1.40 = 2.12 \text{ \AA}$ ²⁵, indicating that this interaction is relatively weak. The Co(1)-O(4)-C(1) angle is $110(3)^\circ$, indicating a near tetrahedral structure. In the structure of the CO sorption complex of $\text{Co}_4\text{Na}_4\text{-A}$, the Co-C-O angle is 180° ¹². In the structure of the CO sorption complex $\text{Ag}_{12}\text{-A}$ ²⁶, the Ag-C-O angle is $105(3)^\circ$ and Ag-C distance is $2.41(4) \text{ \AA}$.

Only one carbon position is found in this work. Therefore, the carbon position must be an averaged one. In this work, the carbon position could not be separated into two different carbon positions. For this reason some of methyl to methyl distances are ill-determined and somewhat short (3.34 \AA) (see Fig. 1).

When methanol is introduced into the dehydrated $\text{Co}_4\text{Na}_4\text{-A}$, not only the Co(II) ions but also the Na^+ ions at Na(2) interact with the gaseous methanol molecules. Each of the 2.5 Na^+ ions at Na(2) is complexed to one methanol oxygen at O(5). The O(5)-C(1) distance $1.98(17) \text{ \AA}$, appears to be somewhat long, but it may be acceptable consi-

dering the estimated standard deviation of this bond. The Na⁺-O distance (2.38(13) Å) is a little shorter than that in the Na⁺-methanol complex (2.47(12) Å)²⁷. This distance is close to the sum of the ionic radius of Na⁺ and the van der Waals radius of oxygen, 0.95 + 1.40 = 2.35 Å²⁵.

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