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부분적으로 Co^{2+} 이온으로 치환된 제올라이트 X, $Co_{41}Na_{10}$-X를 탈수한 결정구조

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Crystal Structure of Dehydrated Partially Cobalt(II)-Exchanged Zeolite X, $Co_{41}Na_{10}$-X

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요 약

부분적으로 Co^{2+} 이온으로 치환된 제올라이트 X ($Co_{41}Na_{10}Al_{92}Si_{100}O_{384}$)를 탈수한 구조를 21 ℃에서 입방공간군 $Fd\bar{3}$ (a = 24.544(1)Å)을 사용하여 단결정 X-선 회절법으로 해석하고 정밀화하였다. 이 결정은 $Co(NO_3)_2$와 $Co(O_2CCH_3)_2$의 농도가 각각 0.025 M 되도록 만든 혼합 용액을 이용하여 흐름법으로 이온 교환하여 만들었다. 이 결정은 380℃에서 2 x 10^{-6} Torr 하에서 2일간 진공 탈수하였다. Full-matrix 최소자승법 정밀화 계산에서 $I > 3\sigma(I)$인 211 개의 독립 반사를 사용하여 최종 오차 인자를 R_1 = 0.059, R_2 = 0.046까지 정밀화시켰다. 이 구조에서 Co^{2+} 이온과 Na^+ 이온은 서로 다른 4개의 결정학적 자리에 위치하고 있었다. 41개의 Co^{2+} 이온은 점유율이 높은 서로 다른 두개의 자리에 위치하고 이었다. 16개의 Co^{2+} 이온은 이중 6-산소 고리 (D6R)의 중심에 위치하였고 (자리 I; Co-O = 2.21(1)Å, O-Co-O = 90.0(4)°), 25개의 Co^{2+} 이온은 큰 동공에 있는 자리 II에 위치하고 세 개의 산소로 만들어지는 평면에서 큰 동공쪽으로 약 0.09 Å 들어간 자리에 위치하고 있었다 (Co-O = 2.05(1)Å, O-Co-O = 119.8(7)°). 10개의 Na^+ 이온은 2개의 서로 다른 자리에 위치하고 있다. 7개의 Na^+ 이온은 큰 동공에 있는 자리 II 위치하였다 (Na-O = 2.29(1)Å, O-Na-O = 102(1)°). 3개의 Na^+ 이온은 큰 동공에 있는 자리 III에 위치하고 있었다 (Na-O = 2.59(10)Å, O-Na-O = 69.0(3)°). 7개의 Na^+이온은 가장 가까운 산소 평면에서 큰 동공 쪽으로 약 1.02Å 들어간 자리에 위치하고 있었다. Co^{2+} 이온은 자리 I과 자리 II에 우선적으로 위치하고, Na^+ 이온은 그 나머지 자리인 자리 II와 자리 III에 위치한다.

Abstract

The crystal structure of dehydrated, partially Co(II)-exchanged zeolite X, stoichiometry $Co_{41}Na_{10}$-X ($Co_{41}Na_{10}Si_{100}Al_{92}O_{384}$) per unit cell, has been determined from three-dimensional X-ray diffraction data gathered by counter methods. The structure was solved and refined in the cubic space group $Fd\bar{3}$: a = 24.544(1) Å at 21(1) ℃. The crystal was prepared by ion exchange in a flowing stream using a solution 0.025 M each in $Co(NO_3)_2$ and $Co(O_2CCH_3)_2$. The crystal was then dehydrated at 380 ℃ and 2 x 10^{-6} Torr for two days. The structure was refined to the final error indices, R_1 = 0.059 and R_2 = 0.046 with 211 reflections for which $I > 3\sigma(I)$. Co^{2+} ions and Na^+ ions are located at the four different crystallographic sites. Co^{2+} ions are located at two different sites of high occupancies. Sixteen Co^{2+} ions are located at the center of the double six-ring (site I; Co-O = 2.21(1) Å and O-Co-O = 90.0(4)°) and twenty-five Co^{2+} ions are located at site II in the supercage. Twenty-five Co^{2+} ions are recessed 0.09 Å into the supercage from its three oxygen plane (Co-O = 2.05(1) Å and O-Co-O = 119.8(7)°). Na^+ ions are located at two different sites of occupancies. Seven Na^+ ions are located at site II in the supercage (Na-O = 2.29(1) Å and O-Na-O = 102(1)°). Three Na^+ ions are statistically distributed over site III, a 48-fold equipoint in the supercages on twofold axes; Na-O = 2.59(10) Å and O-Na-O = 69.0(3)°). Seven Na^+ ions are recessed 1.02 Å into the supercage from the three oxygen plane. It appears that Co^{2+} ions prefer sites I and II in order, and that Na^+ ions occupy the remaining sites, II, and III.

1. Introduction

The zeolite X of isomorph of the mineral faujasite has an open, negatively charged framework. The exchangeable cations can be located on various sites. Some of these sites, in the large cages, are easily accessible, while others are located in the dense cages. The limited dimensions of the apertures which control access to these small cavities are frequently given as a factor limiting the ion exchange.[1,2]

Cation substitution into zeolite X is one of the methods of modification of their physical and chemical properties, so the problem of reactivity and location of multivalent-exchanged ions is of interest from both theoretical and practical points of view. The distribution and coordination of various cations in the framework of faujasite-type zeolites have been widely investigated and reviewed.[3]

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 ion exchanged zeolites. For example, the dehydrogenation of alkanes,[4] the conversion of alcohols to aldehydes and ketones,[5] and the oxidation of n-hexane to carboxylic acids[6-9] have been conducted (usually with yields increased by the exchange) over A- and X-type zeolites containing Cr(II), Mn(II), Fe(II), Co(II), or Ni(II) ions. Intrazeolitic transition metal complexes have also been characterized spectroscopically. By means of reflectance spectroscopy, Klier and Ralek[10,11] studied complexes of Co(II) and Ni(II) with H_2O, NH_3, N_2O, and cyclopropane in A-type zeolite systems. Also, Boudart *et al.*,[12] employing Mossbauer spectroscopy, examined Fe(II) complexes of several small

Table I. [a]Positional, Thermal, and Occupancy Parameters of Dehydrated $Co_{41}Na_{10}$-X.

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	[c]Occupancy fixed
Co(1)	16(c)	0	0	0	5(1)	5(1)	5(1)	3(1)	3(1)	3(1)	16.1(2)	16
Co(2)	32(e)	2193(2)	2193(2)	2193(2)	14(1)	14(1)	14(1)	10(2)	10(2)	10(2)	25.1(3)	25
Na(1)	32(e)	2410(10)	2410(10)	2410(10)	4(5)	4(5)	4(5)	-0(10)	-0(10)	-0(10)	6.7(6)	7
Na(2)	48(f)	4000(100)	1250	1250	14(3)d						2.7(9)	3
Si	96(g)	-520(2)	1217(3)	341(2)	4(1)	5(1)	5(9)	-1(2)	-3(2)	1(2)		96
Al	96(g)	-536(3)	371(2)	1207(3)	8(1)	5(1)	5(1)	-9(2)	5(2)	-7(2)		96
O(1)	96(g)	-1100(5)	18(7)	1055(5)	1.9(3)							96
O(2)	96(g)	-22(7)	-3(7)	1488(4)	2.1(2)							96
O(3)	96(g)	-300(4)	614(6)	588(5)	1.3(2)							96
O(4)	96(g)	-645(5)	845(6)	1674(6)	2.4(3)							96

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

molecules such as N_2, O_2, CO, pyridine, CS_2, and alcohols in Y-type zeolites. Gallezot and Imelik[13-15] present X-ray powder data which show that Ni(II) and Co(II) prefer site I whereas Cu(II) prefers site I′ in dehydrated Y zeolites.

Recently single-crystal X-ray studies on hydrated and dehydrated chabazite[16,17] and heulandite,[18] exchanged under controlled conditions with mono- and di- valent cations, have shown that the extra-framework structure, expecially the cation distribution, may be rationalized, to a large extent, in terms of the size, charge and electronic nature of the exchanged cation. In addition, these studies have shown that the comparison of the electron density maps of the same zeolite, exchanged with different cations, may be useful in determining site locations and possibly the approximate ratio of two different cations at the same site.[18]

This work was initiated to investigate the cation positions in the crystal structure of the dehydrated fully Co^{2+}-exchanged zeolite X. If fully Co^{2+}-exchanged zeolite X could not be obtained, the structural basis of limit would be seen and the site selectivities for two ions (Co^{2+} and Na^+ ion) of different charges would be learned.

2. Experimental Section

Large single crystals of sodium zeolite X, stoichiometry $Na_{92}Al_{92}Si_{100}O_{384}$, were prepared in St. Petersburg, Russia.[19] One of these, a colorless octahedra about 0.2 mm in cross-section was lodged in a fine Pyrex capillary.

$Co_{41}Na_{10}$-X was prepared using an exchange solution in which mole ratio of $Co(NO_3)_2$ and $Co(O_2CCH_3)_2$ was 1 : 1 with a total concentration of 0.05 M. Ion exchange was accomplished by flow methods; the solution was allowed to flow past the crystal at a velocity of approximately 1.5 cm/s for 5 days at 24(1) ℃. The red hydrated crystal was dehydrated at 380 ℃ and 2 x 10^{-6} Torr for 2 days.

After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal has become blue.

The cubic space group $Fd\bar{3}$ was used throughout this work. Diffraction data were collected with an aotomated Enraf-Nonius four-circle computer controlled CAD-4 diffractometer equipped with a

pulse-height analyzer and a graphite monochromator, using Mo Kα radiation (Kα_1, λ = 0.70930 Å, Kα_2, λ = 0.71359 Å). The unit cell constants at 21(1) ℃ determined by least-squares refinement of 25 intense reflections for which 14° < 2θ < 24° are a = 24.544(1) Å.

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

Dehydrated $Co_{41}Na_{10}$-X	
Si-O(1)	1.61(1)
Si-O(2)	1.69(2)
Si-O(3)	1.69(1)
Si-O(4)	1.63(2)
Al-O(1)	1.68(2)
Al-O(2)	1.71(2)
Al-O(3)	1.73(1)
Al-O(4)	1.66(2)
Co(1)-O(3)	2.21(1)
Co(2)-O(2)	2.05(1)
Na(1)-O(2)	2.29(1)
Na(2)-O(4)	2.59(10)
Na(2)-O(1)	3.16(2)
O(1)-Si-O(2)	113.4(8)
O(1)-Si-O(3)	107.5(7)
O(1)-Si-O(4)	113.8(7)
O(2)-Si-O(3)	107.2(6)
O(2)-Si-O(4)	105.5(7)
O(3)-Si-O(4)	112.0(7)
O(1)-Al-O(2)	115.1(8)
O(1)-Al-O(3)	105.1(7)
O(1)-Al-O(4)	112.6(7)
O(2)-Al-O(3)	107.0(7)
O(2)-Al-O(4)	102.5(7)
O(3)-Al-O(4)	114.8(7)
Si-O(1)-Al	127.8(8)
Si-O(2)-Al	129.4(7)
Si-O(3)-Al	120.7(7)
Si-O(4)-Al	159.6(9)
O(3)-Co(1)-O(3)	90.0(4)
O(2)-Co(2)-O(2)	119.8(7)
O(2)-Na(1)-O(2)	102(1)
O(4)-Na(2)-O(4)	69.0(3)
O(1)-Na(2)-O(1)	139.0(11)

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

The ω-2θ scan technique was used. The data were collected using variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.24 and 0.34 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 collection. The intensities of all lattice points for which 2θ < 60° were recorded. Of the 1139 reflections examined, only the 211 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

The intensities were corrected for Lorentz and polarization effects; the resultant estimated standard deviations were assigned to each reflection by the computer programs, GENESIS, PROCESS and WEIGHT.[20]

An absorption correction (uR = 0.172, ρ_{cal} = 1.589 g/cm^3 and F(000) = 6839) was made empirically using a Ψ scan.[21] The calculated transmission coefficients ranged from 0.971 to 0.982. This correction has little effect on the final R indices.

3. Structure Determination

Full-matrix least-squares refinement of dehydrated $Co_{41}Na_{10}$-X was initiated with atomic parameters of the framework atoms [Si, Al, O(1), O(2), O(3) and O(4)] in dehydrated Na_{88}-X.[22] Initial isotropic refinement of the framework oxygen atoms converged to an R_1 index, $(\Sigma||F_o|-|F_c||)/\Sigma F_o)$ of 0.34 and a weighted R_2 index, $(\Sigma\omega(F_o-|F_c|)^2/\Sigma\omega F_o^2)^{1/2}$ of 0.38.

The initial difference Fourier function revealed two large peaks at (0.0, 0.0, 0.0) and (0.222, 0.222, 0.222)

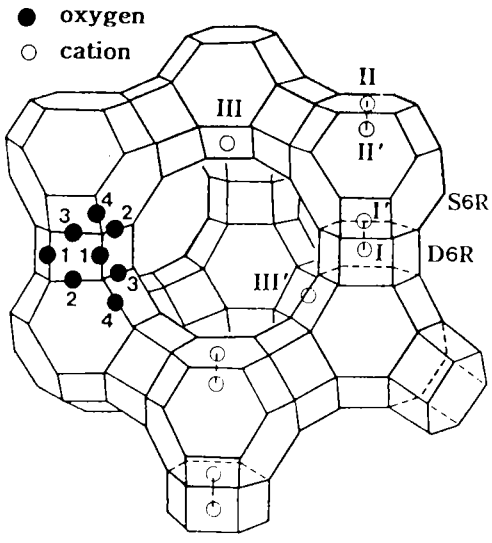


Fig 1. Framework structure of zeolite X. Near the center of the each line segment is an oxygen atom. The different oxygen atoms are indicated by numbers 1 to 4. Silicon and aluminum atoms alternate at the tetrahedral intersection, except that Si substitutes for about of the Al's. Extraframework cation positions are labeled with Roman numerals.

with heights of 11.36 and 6.76 eÅ^{-3}, respectively. These two peaks were stable in least-squares refinement. Anisotropic refinement including these Co^{2+} ions at Co(1) and Co(2) positions converged to R_1 = 0.065 and R_2 = 0.051. Occupancy refinement converged at 16.1(2) and 25.1(3), respectively.

From a subsequent Fourier map, Na^+ ions at Na(1) were located and refined. Na^+ ions at Na(1) and Co^{2+} ions at Co(2) lie on the threefold axes of unit cell. The sum of these two ions can not exceed 32.0. Otherwise unacceptable close interionic distance would occur. Therefore the occupancies of Co(2) and Na(1) were refined with the constrain that the sum of occupancies be 32.0 (see Table 1). These values were reset and fixed at 25.0 Co^{2+} ions at Co(2) and at 7.0 Na^+ ions at Na(1), respectively. Anisotropic refinements fo framework atoms, Al and Si, and Co^{2+} ions at Co(1) and Co(2) and Na^+ ions at Na(1),

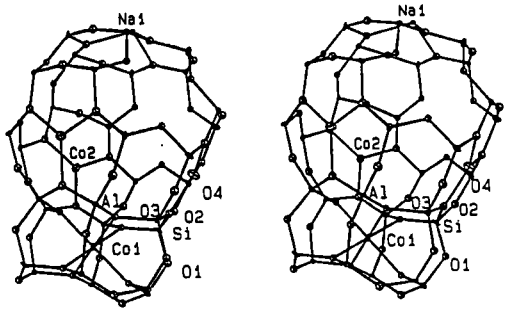


Fig. 2. A stereoview of sodalite cavity of dehydrated $Co_{41}Na_{10}$-X. One Co^{2+} ion at Co(1) lies at site I, three Co^{2+} ions at Co(2) lie at site II, and one Na^+ ions at Na(1) lie at site II. All double six-rings have this arrangement. Ellipsoids of 20% probability are shown.

and isotropic refinement of the framework oxygen atoms converged to R_2 = 0.061 and R_2 = 0.046 (see Table I).

It is not so difficult to distinguish Co^{2+} from Na^+ ions for several reasons. First, their ionic radii are different, Co^{2+} = 0.72 Å and Na^+ = 0.97 Å, and their atomic scattering factors are also different, 25 e^- for Co^{2+} *us.* 10 e^- for Na^+.[23] Secondly, the approach distances between those ions and zeolite oxide ions in the previous dehydrated Co_4Na_4-A[24] (see Table I and II) and Na_{88}-X[22] have been determined and are indicative. Finally, the requirement that 92 monovalent metal ion(or 46 divalent metal ion) per unit cell be found do not allow the major positions to refine to acceptable occupancies with the alternative assignment of ionic identities

From a successive difference Fourier, one peak was found at (0.401, 0.125, 0.125), height = 0.61 eÅ^{-3}, which refined as Na(2). Simultaneous positional occupancy, and anisotropic thermal parameter refinement converged to the error indices R_1 = 0.059 and R_2 = 0.045. The occupancy num,ber of Co(1), Co(2), Na(1), and Na(2) were reset and fixed as in the last column of Table I.

All shifts in the final cycles of least-squares refinement were less than 0.1% of their corresponding standard deviations. The final error indices onverged to R_1 = 0.059 and R_2 = 0.046. The final difference function was featureless except for a peak at (0.025, 0.129, 0.961) of height 0.57 eÅ^{-3}. This peak was not within bonding distance of any other atom, and was not considered further.

All crystallographic calculations were done using the MolEN (a structure determination package programs supplied by Enraf-Nonius). The full-matrix least-squares program used minimized $\Sigma\omega(F_o-|F_c|)^2$; the weight ($\omega$) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[25,26] for Si, Al, O^-, and Co^{2+} and Na^+ were used. All scattering factors were modified to account for anomalous dispersion.[27] The final structural parameters and selected interatomic distances and angles are presented in Tables I and II, respectively.

4. Discussion

The basic building unit of zeolite X can be considered to be the sodalite cavity, truncated octahedron of composition $Si_{12}Al_{12}O_{36}$. The sodalite units are arranged tetrhedrally in space like the carbon atoms in diamond. They are joined at alternation 6-oxygen rings by six bridging oxygen atoms. This leads to the existence of small double 6-ring (D6R) cavities and large supercages.[28,29] Each unit cell contains eight supercages, eight sodalite units, and sixteen double 6-rings.

There are exchangeable cations which balance the negative charge of the aluminosilicate framework located within cavities. The exchanged cations can be located on various sites; site I in a hexagonal prism (double 6-ring), site I′ near the single 6-ring entrance to a hexagonal prism in the sodalite (β) cavity, II′ inside the sodalite cavity near the single 6-ring (S6R) entrances to the large (α) cavity, II in the supercages adjacent to S6R, III in supercages opposite O(3) and O(4) ring of 4-ring, and III′ somewhat off III (off the twofold axis) (see Figure 1).

In this structure, forty-one Co^{2+} ions are located at two different crystallographic sites. Sixteen Co^{2+} ions at Co(1) lie at site I in the center of a double six-oxygen ring (D6R) (see Figure 2). This 16-fold position is fully occupied. Each Co^{2+} ion at Co(1) is coordinated by six O(3) oxygen atoms of hexagonal prism at distance of 2.21(1) Å, which is longer than the sum of the ionic radii of Co^{2+} and O^{2-}, 0.72 + 1.32 = 2.04 Å.[23] This distance is very similar to the distance of the previous Co^{2+} ions in the structure of Co_4Na_4-A.[24]

The Co^{2+} ions are not found at site I′, on a threefold axis in the sodalite unit opposite a double six-ring (D6R's). The closest site I to site I′ may be about 3.0 Å. If a D6R has a Co^{2+} ion in it, its two adjacent sites, I′'s, must be unoccupied because of electrostatic requlsive force of cations.

The twenty-five Co^{2+} ions at Co(2) are located at site II in the supercage (see Figures 2 and 3). This is 32-fold position, but it is only twenty-five occupied. The Co(2)-O(2) distance, 2.05(1) Å, is almost the same as the sum of ionic radii of Co^{2+}

Table III. Deviations of Atoms (Å) from the 6-ring planes.

		Dehydrated $Co_{41}Na_{10}$-X
at O(3)[a]		
	Co(1)	-1.27(1)
at O(2)[b]		
	Co(2)	0.09(1)
	Na(1)	1.02(1)

[a]A negative deviation indicates that the atom lies in the D6R.

[b]A positive deviation indicates that the atom lies in the supercage.

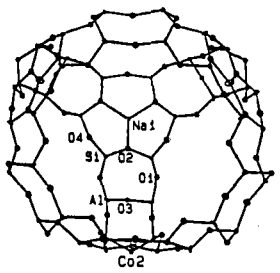
and O^{2-}. These Co^{2+} ions are slightly recessed, 0.09(1) Å, into the supercage from the plane of the three O(2) oxygens (see Table Ⅲ). The O(2)-Co(2)-O(2) bond angle, 119.8(7)° , is nearly trigonal planar.

In this structure, ten Na^+ ions are located at two different crystallographic sites. Seven Na^+ ions at Na(1) lie at site Ⅱ and are recessed 1.02 Å into the supercage from the single 6-ring plane at O(2). Each these ions coordinates to three O(2) oxygens at 2.29(1) Å, is almost the same as Na^+ the sum of Na^+ and O^{2-} radii, 0.95 + 1.32 = 2.27 Å.[23] The angle subtended at Na(1), O(2)-Na(1)-O(2) is 102(1)°. This (site Ⅱ) is 32-fold position, but it is only seven occupied. The Co(2) and Na(1) positions are both 32-fold positions, but the sum of these two ions can not exceed 32. Otherwise Na^+-Co^{2+} distance will be very close.

Three Na^+ ions at Na(2) occupy the 48-fold position at site Ⅲ in the supercage (see Figure 3). About 37.5% of supercages have one Na^+ ion at Na(2) and the remainder, about 62.5% of supercages, have not any Na^+ ion at Na(2). The Na(1)-O(4) distance, 2.59(10) Å, is longer than the sum of the corresponding ionic radii, 0.95 1.32 = 2.27 Å.[23]

Recently the crystal structures of dehydrated Ca_{46}-X,[30] Cd_{46}-X,[31] Sr_{46}-X,[32] Mn_{46}-X,[32] Mg_{46}-X,[32] Ba_{46}-X,[33] and $Ca_{32}K_{28}$-X[30] have been determined. The divalent cations, Ca^{2+}, Cd^{2+}, Sr^{2+}, and Mn^{2+} ions are located at two different sites of high occupancies: sixteen at site Ⅰ and thirty at site Ⅱ. In the crystal structures of the Ba_{46}-X and Mg_{46}-X, Ba^{2+} and Mg^{2+} ions are located at the three different sites; fourteen at site Ⅰ, two at site Ⅰ′, and thirty at site Ⅱ. In the crystal structure of $Ca_{32}K_{28}$-X, smaller Ca^{2+} ions occupy the smaller pore site (16 at site Ⅰ and 16 at site Ⅱ) and larger K^+ ions occupy deep in the supercage (16 at sites Ⅱ and 12 at Ⅲ). In present work, all Co^{2+} ions are located in the centers of double six ring (site Ⅰ) and near the plane of single six-oxygen rings inside the supercage (site Ⅱ). Therefore. the present structure is in good agreement with the previous works.

In summary, this work indicates that most of the Na^+ ions in zeolite X can be exchanged by Co^{2+} ions. The smaller and more highly charged Co^{2+} ions fill the site Ⅰ position, with the remainder going to site Ⅱ. affirming that Co^{2+} ions prefer site Ⅰ. The large Na^+ ions, which are less able to balance the anionic charge of the zeolite framework because of their larger size and smaller charge, avoid D6R's and finish filling site Ⅱ, with the remainder going to the least suitable cation site in lthe structure, site



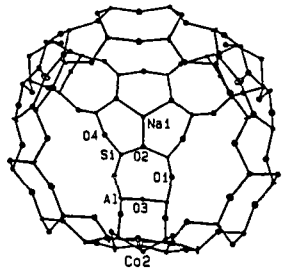
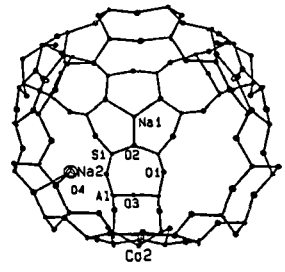


Fig. 3. A stereoview of supercage of dehydrated $Co_{41}Na_{10}$-X. One Co^{2+} ion at Co(2) lies at site Ⅱ and one Na^+ ions at Na(1) lie at site Ⅱ. Ellipsoids of 20% probability are shown.



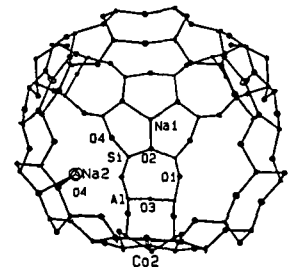


Fig. 4. A stereoview of supercage of dehydrated $Co_{41}Na_{10}$-X. three Co^{2+} ions at Co(2) lie at site Ⅱ, one Na^+ ions at Na(1) lie at site Ⅱ, and one Na^+ ions at Na(2) lie at site Ⅲ. Ellipsoids of 20% probability are shown.

Ⅲ. In this structure all Co^{2+} and Na^{+} ions are located in the sites Ⅰ, Ⅱ, and Ⅲ. The Co^{2+} ions are not found in the sites Ⅰ′ and Ⅱ′.

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