카드뮴 이온으로 완전히 치환한 제올라이트 A를 진공 탈수한 구조와 이것에 요오드를 흡착한 결정구조

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Crystal Structures of Vacuum Dehydrated Fully Cd^{2+}-Exchanged Zeolite A and of Its Iodine Sorption Complex

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요 약

Cd^{2+} 이온으로 이온교환된 제올라이트 A를 650 °C에서 2×10^{-6} T orr의 진공하에서 탈수한 구조 (a = 12.189(2) A)와 이 결정에 요오드가 흡착된 구조 (a = 12.168(2) A)를 21 °C에서 입방공간군 Pm3m를 사용하여 단결정 X-선 회절법으로 해석하고 정밀화하였다. 탈수한 Cd$_6$-A의 구조는 Full-matrix 최소자승법 정밀화 계산에서 I > 3σ(I)인 186개의 독립반사를 사용하여 최종오차인자를 R$_1$ = 0.057, R$_2$ = 0.063 까지 정밀화 계산하였고, 이 결정을 요오드로 흡착시킨 구조는 181 개의 독립 반사를 사용하여 R$_1$ = 0.082, R$_2$ = 0.085까지 정밀화켰다. 두 결정에서 단위세포당 6개의 Cd^{2+} 이온은 서로 다른 2개의 3회 회전축상에 위치하고 있었다. 요오드가 흡착된 구조에서 4개의 Cd^{2+} 이온

은 O(3)의 (111) 평면에서 큰 동공쪽으로 약 0.69(1) Å 들어가서 I_3^- 와 결합하고 있고 나머지 2개의 Cd^{2+} 이온은 O(3)의 (111) 평면에서 소다라이트 동공 깊숙히 약 0.68(1) Å 들어간 자리에 위치 하고 있다. 단위세포당 약 4개의 I_3^- 이온이 큰 동공내에 흡착되었다. 각각의 I_3^-는 6-링 Cd^{2+}와 골조의 8-링 산소에 다리를 놓고 있으며 O(1)-I(1)-I(2) 각도는 172(1)° 로써 거의 선형이고 약한 전하이동 착물을 골조의 8-링 산소와 이루고 있다. 큰 동공 내에 존재하는 I_3^- 이온은 부분적으로 탈수된 Cd_6-A에서 요오드 증기와 물분자가 반응하여 H^+ 이온과 I^- 이온이 생성된후 다시 I^- 이온과 I_2 분자와 반응하여 생성되었을 것이다.

Abstract

The crystal structure of dehydrated fully Cd^{2+}-exchanged zeolite A evacuated at 2×10^{-6} Torr and 650 °C (a = 12.189(2) Å) and of its iodine sorption complex (a = 12.168(2) Å) have been determined by single crystal x-ray diffraction techniques in the cubic space group $Pm\bar{3}m$ at 21(1) °C. The structures were refined to final error indices, R_1 = 0.057 and R_2 = 0.063 with 186 reflections and R_1 = 0.082 and R_2 = 0.085 with 181 reflections, respectively, for which $I > 3\sigma(I)$. In both structures, six Cd^{2+} ions lie at two distinguished threefold axes of unit cell. In the crystal structure of an iodine sorption complex of Cd_6-A, four Cd^{2+} ions are recessed 0.69(1) Å into the large cavity to complex each with I_3^- from the (111) plane of O(3), whereas two Cd^{2+} ions recessed 0.68(1) Å into the sodalite unit. Approximately 4.0 I_3^- ions per unit cell are sorbed. Each bridge between a Cd^{2+} ion and 8-ring oxygens ((I-I-I)$^-$ = 117(1)° and O(1)-I(1)-I(2) = 172(1)). The near-linear I-I-O angle and its interatomic distance (I-O = 3.57(3) Å) are indicative of a weak charge transfer interaction between the framework oxygen and iodine. The existence of I_3^- inside the large cavity indicates that the H^+ ions and I^- ions may be produced by reaction of I_2 vapor with water molecules which may be associated with Cd^{2+} ions in partially dehydrated Cd_6-A. I_3^- ions may be produced by the combination of I^- and I_2.

Introduction

Zeolites can sorb various kinds of molecules. In particular, dihalogens are readily absorbed by zeolite to complex by a variety of mechanisms. The crystal structures of a bromine sorption complex of Na_{12}-A,[1] a iodine sorption complex of Ca_4Na_4-A,[2] and a chlorine sorption complex of Ag_{12}-A[3] have been reported. About six bromine molecules per unit cell were sorbed into the bromine sorption complex of Na_{12}-A. However, these bromine molecules appeared to interact neither with the anionic framework nor with Na^+ ions. On the other hand, in the crystal structure of an iodine sorption complex of Ca_4Na_4-A, the 5.65 diiodine molecules were sorbed per unit cell forming charge-transfer complexes with framework 8-ring oxygens (O-I-I = 178 °).[4,5] Chlorine gas also oxidizes haxasilver to AgCl as observed in the structure of a chlorine sorption complex of dehydrated, fully Ag^+-exchanged zeolite A.[3] Additional six dichlorine molecules per unit cell are sorbed and formed charge-transfer complexes with framework oxide ions (O-Cl-Cl = 166(2)°).

Recently, several structures of halogen sorption complexes of dehydrated, partially cobalt(II) - exchanged have been determined. In the crystal structure of a Cl_2 sorption complex of Co_4Na_4-A,[6] four chlorine molecules act as ligands to coordinate each to one Co(II) ion, in a bent manner. Dehydrated $Co_{3.5}Na_5$-A can sorb upto 5.0 diiodine molecules[7] per unit cell. In the crystal structure of a bromine sorption complex of dehydrated partially cobalt(II)-exchanged zeolite A,[8] a redox reaction was apparently occurred between Co(II) and Br_2 to yield Co(III) and Br_3^- ions. The 4 Na^+ and 4 Co^{3+} ions per unit cell occupy 6-ring sites on 3-fold axes. Four quite asymmetric Br_3^- ions, each briges between a Co^{3+} ion and an 8-ring framework oxygens

((Br~Br~Br)⁻ = 138° and Br~Br~O = 177°). 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.

This work was initiated to investigate the cation positions in the crystal structure of the fully Cd(II)-exchanged zeolite A which was dehydrated at 650°C. The crystal structure of a iodine sorption complex of dehydrated Cd_6-A has been determined to locate the sorbed iodine molecules within the zeolite, and to observe the reactivity of iodine molecule within the zeolite.

Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method.[9] Each of two single crystals about 85 μm on edge was selected and lodged in a fine quartz capillary. An exchange solution of $Cd(NO_3)_2$ and $Cd(OOCCH_3)_2$ in the mole fraction of 1 : 1 with a total concentration 0.05 M was allowed to flow past each crystal at a velocity of approximately 1.5 cm/sec for 3 d. Each crystal was washed for 1 h with distilled water at 80 °C.

Each crystal, placed in a finely drawn quartz capillary, was attached to a vacuum system and cautiously dehydrated by gradually increasing its temperature (ca. 25 °/h) to 650 °C at a constant pressure of 2 x 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 iodine complex, the dehydrated Cd_6-A crystal was treated with 312 Torr zeolitically dried iodine vapor for 24 hrs at 150 °C. The colorless dehydrated crystal had become black after exposure to iodine vapor. After about 24 h, the crystal, still in its iodine atomsphere, 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 discussed previously.[10,11] 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 Kα radiation (Kα_1, λ = 0.70930 Å, Kα_2, λ = 0.71359 Å). In each case, the unit cell constants at 21(1) °C determined by least squares refinement of 25 intense reflections for which $18° < 2\theta < 25°$ are a = 12.189(2) Å for Cd_6-A and a = 12.168(2) Å for the iodine sorption complex of Cd_6-A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $0 \le h \le k \le l$ and lhk, $0 \le l \le h \le k$) were examined. The intensities were measured using ω-2θ scan technique over a scan width of $(0.80 + 0.344 \tan\theta)°$ in ω. The data were collected using the variable scan speeds. Most reflections were observed at slow scan speeds, ranging between 0.25° and 0.32° 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 stablity. Only small, random fluctuations of these check reflections were noted during the course of data collections. For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70°$ were recorded. Only those of which $I > 3\sigma(I)$ were used for structure solution and refinement. These amounted to 186 of the 858 reflections for the first crystal, and 181 of the 853 reflections for the second crystal, respectively.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard diviations were assigned to each averge reflection by the computer programs, PAINT and WEIGHT.[12]

An absorption correction (μR = 0.090, ρ_{cal} = 1.408 g/cm^3 and F(000) = 990 for the first crystal, and μR = 0.313, ρ_{cal} = 3.337 g/cm^3 and F(000) = 1626 for the second crystal) was to be negligible and was not applied.[13]

Structure Determination

(a) Dehydrated Cd$_6$-A at 650℃ 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)] of vacuum dehydrated Cd$_6$-A at 450 ℃.[14] Anisotropic refinement of the framework atoms converged to an R_1 index, $(\Sigma|F_o-|F_c||)/\Sigma F_o$ of 0.394 and a weighted R_2 index, $(\Sigma w(F_o-|F_c|)^2/\Sigma w F_o^2)^{1/2}$ of 0.506.

The initial difference Fourier function revealed one large peak at (0.166, 0.166, 0.166) of height of 11.79(19) e A^{-3}. This peak was stable at least − squares refinement.

Anisotropic refinement of the framework atoms and isotropic refinement of the Cd^{2+} ions lowered the error indices to R_1 = 0.079 and R_2 = 0.076.

The occupancy number of Cd^{2+} ions per unit cell was refined to Cd = 5.91(5). The thermal ellipsoids of the threefold-axis Cd^{2+} ions became very elongated in subsequent refinements, indicatating the presence of two nonequivalent Cd^{2+} ions at this position. These were refined at x = 0.16 and x = 0.19 on the threefold axes (see Table I). The occupancy numbers of Cd^{2+} ions at Cd(1) and Cd(2) per unit cell were refined to Cd(1) = 2.87(5), and Cd(2) = 2.89(4). These were fixed at Cd(1) = 3.0, Cd(2) = 3.0, respectively because the cationic charge should be exceeded +12 per Pm3m unit cell. Anisotropic refinement of the framework atoms and Cd^{2+} ions converged to R_1

Table I. [a]Positional, Thermal, and Occupancy Parameters

Crystal 1. Dehydrated Cd$_6$-A at 650 ℃

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B$_{iso}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(k)	0	1826(5)	3683(4)	24(3)	26(3)	19(3)	0	0	9(7)		24.0[d]
O(1)	12(h)	0	2000(10)	5000	60(20)	30(10)	60(20)	0	0	0		12.0
O(2)	12(i)	0	2940(9)	2940(9)	40(10)	40(8)	40(8)	0	0	40(20)		12.0
O(3)	24(m)	1109(3)	1109(3)	3266(9)	42(6)	42(6)	40(10)	20(20)	0(10)	0(10)		24.0
Cd(1)	8(g)	1943(3)	1943(3)	1943(3)	43(2)	43(2)	43(2)	14(6)	14(6)	14(6)	2.87(5)	3.0
Cd(2)	8(g)	1588(4)	1588(4)	1588(4)	58(3)	58(3)	58(3)	50(7)	50(7)	50(7)	2.89(4)	3.0

Crystal 2. Iodine Sorption Complexes of Dehydrated Cd$_6$-A

Atom	Wyc. Pos.	x	y	z	[b]β_{11} B$_{iso}$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[c]Occupancy varied	fixed
(Si,Al)	24(k)	0	1810(7)	3673(6)	35(5)	18(4)	6(4)	0	0	7(9)		24.0[d]
O(1)	12(h)	0	2010(20)	5000	100(30)	50(30)	10(20)	0	0	0		12.0
O(2)	12(i)	0	2960(10)	2960(10)	50(20)	30(10)	30(10)	0	0	50(30)		12.0
O(3)	24(m)	1112(8)	1112(8)	3250(10)	22(7)	22(7)	60(10)	20(20)	-20(20)	- 20(20)		24.0
Cd(1)	8(g)	2151(4)	2151(4)	2151(4)	64(4)	64(3)	64(3)	68(7)	68(7)	68(7)	3.76(7)	4.0
Cd(2)	8(g)	1502(7)	1502(7)	1502(7)	35(4)	35(4)	35(4)	40(10)	40(10)	40(10)	1.77(6)	2.0
I(1)	12(1)	1410(10)	4580(10)	5000	140(10)	140(20)	130(20)	-110(30)	0	0	4.18(6)	4.0
I(2)	24(1)	2740(30)	3630(30)	5000	700(100	230(40)	440(50)	0(100)	0	0	4.03(11)	4.0
I(3)	24(m)	2980(20)	3730(20)	3730(10)	310(30)	410(20	410(20)	-240(30)	-240(30)	-240(30)	4.02(10)	4.0

[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]Occupancy for (Si) =12; occupancy for (Al) = 12.

= 0.057 and R_2 = 0.063 (see Table I). In the final cycle of least-squares refinement, all shifts in atomic parameters were less than 0.3 % of their corresponding standard deviations. The final difference function was featureless except one at (0.0, 0.0, 0.0) with peak height of 3.50(73) $e\text{Å}^{-3}$. This peak was not refined at the least-squares refinement.

(b) Iodine sorption complexes of the dehydrated Cd_6-A
Initial full-matrix least-squares refinement was initiated by using the atomic parameters of framework atoms from the previous crystal of Cd_6-A.[14] Anisotropic refinement of the framework atoms converged to R_1 = 0.49 and R_2 = 0.65, respectively.

The initial difference Fourier function revealed two large threefold axis peaks at (0.220, 0.220, 0.220) and (0.139, 0.139, 0.139) with heights of 19.25(33) $e\text{Å}^{-3}$ and 7.07(33) $e\text{Å}^{-3}$, respectively. This peak was stable in the least-squares refinement. Anisotropic refinement including these Cd^{2+} ions at Cd(1) and Cd(2) positions converged to R_1 = 0.315 and R_2 = 0.369. The occupancy numbers of Cd^{2+} ions per unit cell were refined to Cd(1) = 3.8(1) and Cd(2) = 1.8(1). These were fixed at Cd(1) = 4.0 and Cd(2) = 2.0.

A subsequent difference fourier synthesis revealed two large peaks at (0.109, 0.5, 0.5) and (0.277, 0.304, 0.5) with a peak height of 5.30(19) $e\text{Å}^{-3}$ and 3.62(19) $e\text{Å}^{-3}$, respectively. These peaks were stable in least-squares refinement. Including these peaks as I(1) and I(2) lowered the error indices to R_1 = 0.156 and R_2 = 0.165 (see Table I). The occupancy numbers of iodines at I(1) and I(2) were refined to I(1) = 4.18(6) and I(2) = 4.03(11), respectively. These were reset and fixed at I = 4.0. It is furthermore reasonable that these two occupancies should be equal because the distance involved indicates that these positions represent diiodine molecules (see Table I).

Successive difference Fourier map revealed the iodine position I(3) at (0.332, 0.332, 0.359) with a peak height of 2.98(21) $e\text{Å}^{-3}$. The occupancy number of I(3) and Cd(1), and their interatomic distances indicated that these are

associated with each other. Therefore the occupancy of I(3) was fixed at 4.0, the same number as Cd(1) (see Table I). Inclusion I(3) in a least-squares refinement lowered to R_1 = 0.082 and R_2 = 0.085.

The final difference function was featureless except 2.75(86) $e\text{Å}^{-3}$ 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 $\Sigma w(F_o-|F_c|)^2$; the weight(w) of an observation was the reciprocal square of $\sigma(F_o)$, its standard deviation. Atomic scattering factors[15] for Cd^{2+}, I^0, 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 anomalous dispersion correction.[16,17] The final structureal parameters and selected interatomic distances and angles are presented in Table I and II, respectively.

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

	Crystal 1	Crystal 2
(Si,Al)-O(1)	1.620(5)	1.633(8)
(Si,Al)-O(2)	1.632(8)	1.64(1)
(Si,Al)-O(3)	1.688(6)	1.678(8)
Cd(1)-O(3)	2.160(9)	2.23(1)
Cd(2)-O(3)	2.21(1)	2.23(1)
Cd(1)-I(3)		2.90(1)
I(3)-I(2)		2.74(4)
I(2)-I(1)		2.72(3)
I(1)-O(1)		3.57(3)
I(1)-O(2)		3.61(1)
O(1)-(Si,Al)-O(2)	116.0(7)	114(2)
O(1)-(Si,Al)-O(3)	111.5(5)	112.1(7)
O(2)-(Si,Al)-O(3)	105.3(3)	105.5(5)
O(3)-(Si,Al)-O(3)	106.4(4)	107.5(6)
(Si,Al)-O(1)-(Si,Al)	165.0(1)	163(2)
(Si,Al)-O(2)-(Si,Al)	157.4(6)	154.1(8)
(Si,Al)-O(3)-(Si,Al)	137.6(6)	136.3(9)
O(3)-Cd(1)-O(3)	118.8(2)	111.0(4)
O(3)-Cd(2)-O(3)	114.9(2)	111.1(3)
O(1)-Cd(1)-I(3)		113.2(9)
Cd(1)-I(3)-I(2)		115(1)
O(1)-I(1)-I(2)		172(1)
O(2)-I(1)-I(2)		157.3(7)
I(1)-I(2)-I(3)		117(1)

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

Discussion

In the crystal structure of vacuum dehydrated Cd_6–A at 650 °C, all six cd^{2+} ions are found on two different three fold axis sites (Table I and Figure 1). About 2.5 Cd^{2+} ions at Cd(1) extended 0.24 Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.160(9) Å in a slightly distorted trigonal planar arrangement. About 2.5 Cd^{2+} ions at Cd(2) are recessed 0.51 Å into the sodalite unit from the O(3) planes of the 6-ring. Each of these Cd^{2+} ions at Cd(2) is coordinated to three O(3) framework oxygens at 2.21(1) Å.

In the crystal structure of a iodine sorption complex of dehydrated fully Cd(II) exchanged zeolite A, all six Cd^{2+} ions are found on two different three axis sites of unit cell. About 4.0 ions at Cd(II) extended 0.69 Å into the large cavity from the (111) plane at O(3) and are coordinated to three O(3) oxygens at 2.23(1) Å. These Cd^{2+} ions are also complexed with iodine species at I(3). About 2.0 Cd^{2+} ions are recessed 0.68 Å into the sodalite unit from the O(3) plane of the 6-ring. Each of these Cd^{2+} ions is coordinated to three O(3) framework oxygens at 2.23(1) Å. The length of the Cd(1)–O(3) bond has increased from 2.160(9) Å in the vacuum dehydrated structure to 2.23(1) Å in iodine sorption structure. Also the O(3)–Cd(1)–O(3) bond angle changes

from a near trigonal planar value of 118.8(2)° in vacuum dehydrated Cd_6–A to 111.0(4)° in iodine complex, a value closer to tetrahedral. Figures 2 and 3 illustate the coordination environment of the Cd^{2+} ions.

The number of iodine atom or ion at I(i), i = 1-3, are 4.0, 4.0, and 4.0. These iodine species are all located inside the large cavity. They may be placed within their equipoints of partial occupancy. They are rather close to each other : I(1)–I(2) = 2.72(3) Å and I(2)–I(3) = 2.74(4) Å. Their occupancies and interatomic distances suggest that 4.0 I_3^- ((I(1)–I(2)–I(3))$^-$) is formed per unit cell (see Figure 2 and 3).

The existance of I_3^- inside the large cavity indicate that the H^+ ions and I^- ions may be produced by reaction of I_2 vapor with water molecules which may be associated with Cd^{2+} ions in partially dehydrated Cd_6–A.[18,19] I_3^- ions may be produced by the combination of I^- and I_2. These I_3^- ions are asymmetric in bond length and bent (I(1)–I(2)–I(3) = 117(1)° (see Table 2). I_3^- ions have previously been found to be sometimes symmetric and sometimes asymmetric.[20,21] Also the overall length of I_3^- ions, which have been studied in most detail, is approximately 0.5 Å more than twice the single bond length.[20] In the crystal structure of cesium triiodine, the following geometry is reported: I(1)–I(2) = 2.83 Å and I(2)–I(3) = 3.03 Å.[22] For comparison, the I–I distance in free dibromine is 2.662 Å.[23] Each I_3^- ion interacts and
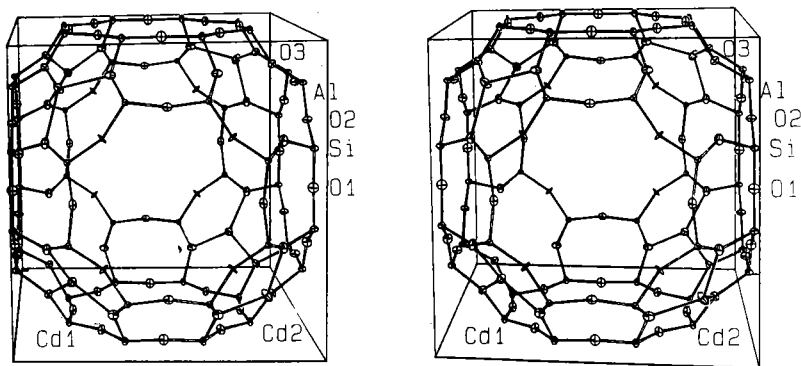

Figure 1. A stereoview of large cavity of vacuum dehydrated Cd_6–A at 650 °C. Three Cd^{2+} ions at Cd(1) and three Cd^{2+} ions at Cd(2) are shown. Ellipsoids of 20 % probability are shown.

stabilizes by complexing with a Cd^{2+} ion and framework oxide ions, O(1) and O(2). The I(1) to O(1) and I(1) to O(2) distances (3.57(3) Å and 3.61(1) Å, respectively) agree well with the sum of van der Walls radii of I and O, 3.55 Å.[24] Also the bond of O(1)-I(1)-I(2) = 172(1)° and that of O(2)-I(1)-I(2) = 157.3(7). The near-linear I-I-O angle is indicative of a weak charge transfer interaction. The bonding distance between Cd^{2+} ions at Cd(1) and I species at I(3) is 2.90(1) Å. This distances is much shorter than the sum of the van der Waals radius of I and the ionic radius of Cd^{2+} (3.12 Å),[25] and also shorter

than the sum of the ionic radii of Cd^{2+} and I^- (3.17 Å).[25]

The present structure is very different from that of a iodine sorption complex of dehydrated Ca_6-A.[26] In this structure, diiodine molecule makes no significant approach to Ca^{2+} ions. In closest approach I-Ca^{2+} distance is 4.025(8) Å. The closest approach of the I(1) position to the framework atom is to O(1).

The result of the present work is very similar to that of bromine sorption complexes of vacuum dehydrated Cd_6-A.[27] In this structure, each 4.5 Cd^{2+} ions is recessed ca. 0.441 Å into the large cavity to complex either with

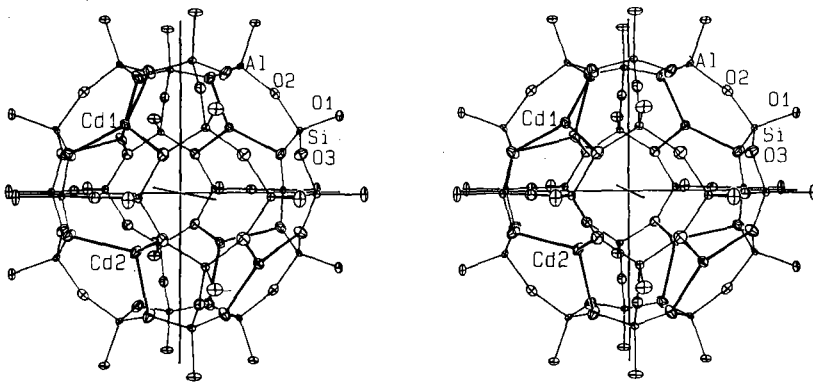Figure 2. A steroview of the sodalite unit of dehydrated Cd_6-A. Three Cd^{2+} ions at Cd(1) and Three Cd^{2+} ions at Cd(2) are shown. Ellipsoids of 20 % probility are used.
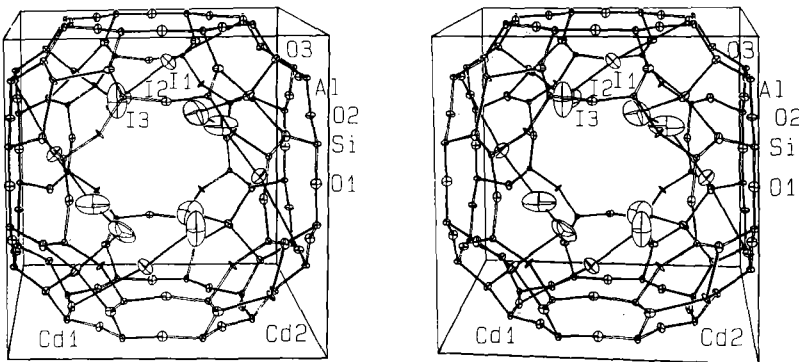

Figure 3. The stereoview of large cavity of a iodine sorption complex of dehydrated Cd_6-A. Ellipsoids of 20 % probability are used.
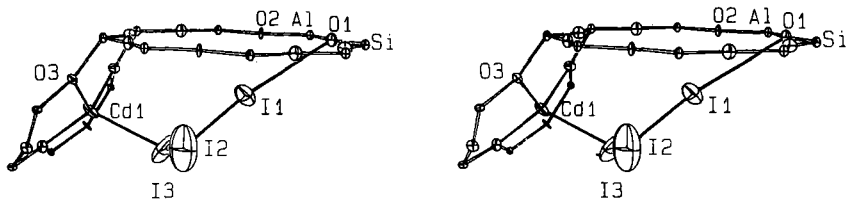
Figure 4. Stereview of one corner of the large cavity showing the I_3^- ions coordinated to Cd^{2+} ion at Cd(1). Ellipsods of 20 % probalility are used.

Table III. Deviations of Atoms(A) from (111) Plane at O(3)

	Crystal 1	Crystal 2
O(2)	0.28(1)	0.29(1)
Cd(1)	0.24(1)	0.69(1)
Cd(2)	−0.51(1)	−0.68(1)
I(3)		3.49(2)

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

Br_5^- or with Br_3^- from the (111) plane of O(3), whereas each 1.5 Cd^{2+} ions are sorbed per unit cell. Each Br_5^- ion interacts and stabilized by complexing with two Cd^{2+} ion and framework oxygens, while each Br_3^- ion interacts with one Cd^{2+} ion and framework oxygens.

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