Two Crystal Structures of Tl$^+$ and Zn^{2+} Exchanged Zeolite A, Tl$_{12-2x}$Zn$_x$–A (x= 4.3 and 3.25)

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The structures of Tl$_{12-2x}$Zn$_x$–A (x = 4.3 and 3.25), vacuum dehydrated zeolite A with all Na$^+$ ions replaced by Tl$^+$ and Zn^{2+} as indicated, have been determined by single-crystal X-ray diffraction techniques in cubic space group *Pm3m* at 21(1) °C (a = 12.100(2) Å for Tl$_{3.4}$Zn$_{4.3}$–A and a = 12.092(2) Å for Tl$_{5.5}$Zn$_{3.25}$–A). The crystals of Tl$_{3.4}$Zn$_{4.3}$–A and Tl$_{5.5}$Zn$_{3.25}$–A were prepared by flow method using exchange solutions in which mole ratios of TlNo$_3$ and Zn(NO$_3$)$_2$ were 1:50 and 1:1, respectively, with total concentration of 0.05M. The structures of the dehydrated Tl$_{3.4}$Zn$_{4.3}$–A and Tl$_{5.5}$Zn$_{3.25}$–A were refined to yield the final error indices R_1 = 0.075 and R_2 = 0.075 with 236 reflections, and R_1 = 0.057 and R_2 = 0.064 with 202 reflections, respectively, for which $I > 3\sigma(I)$. Both structures indicate that Zn(II) ions are coordinated by three framework oxygens: the Zn(II) to O(3) distances are 2.08(1) Å for Tl$_{3.4}$Zn$_{4.3}$–A and 2.07(1) Å for Tl$_{5.5}$Zn$_{3.25}$–A, respectively. In each structure, the angle subtended at Zn(II), O(3)–Zn(II)–O(3) is 119.9(3)° for Tl$_{3.4}$Zn$_{4.3}$–A, and 120.0(3)° for Tl$_{5.5}$Zn$_{3.25}$–A, respectively, close to the idealized trigonal-planar value. Zn(II) ions prefer to 6-ring sites. Tl$^+$ ions do not have any preference to a particular site but occupy simultaneously both at the 6-ring sites and 8-ring sites.

Introduction

The physicochemical properties of zeolite are influenced by the exchangeable cations.[1] Numerous structural studies of the transition metal ions exchanged zeolite A have recently carried out crystallographically.[2-5]

In zeolite A, the cations in 8-ring sites may block three dimensional channel systems. The 8-ring sites population is indeed critical since there should be some obstructions to free diffusion when *ca.* 77% of these windows are filled with cations.[6] Takaishi and Ohgushi eported that one Ca$^+$ ion of Ca$_6$-A[7] per unit cell occupies the 8-ring site and because of this 8-ring cation, Ca$_6$-A is useful for an isomerization catalyst of 1-butene to trans-and cis-2-butenes.[8] However, Pluth and Smith reported that an 8-ring cation is not a Ca^{2+} ion but a K$^+$ ion due to the impurity from exchange solution.[9,10]

Raghavan and Seff determined the crystal structure of partially dehydrated Zn$_5$K$_2$-A.[11] Five Zn^{2+} ions per unit cell occupy three nonequivalent positions, all on the unit cell threefold axes, near the centers of 6-ring. The K$^+$ ions show a distinct preference for 8-ring sites (one in the 8-ring plane and the other near that plane), despite of the presence and ready availability of vacant 6-ring sites.

Up to this time, no structural studies of mixed cation system of zeolite A exchanged with Tl$^+$ and Zn^{2+} ions have been reported. This study was initiated to investigate the geometry of the partial "blockage" of the large 8-ring pore[12] of zeolite by Tl$^+$ ions. It would be also interesting to learn the selective positions of Tl$^+$ and Zn^{2+} ions in the crystal structures of variously Tl$^+$ and Zn^{2+} exchanged zeolite A. Because of the high scattering powers of Tl$^+$ and Zn^{2+} ions, the precise and reliable crystallographic determinations should be easy to achieve.

Experimental Section

Sample Preparation. Single crystals of the synthetic molecular sieve zeolite 4A, Na$_{12}$Si$_{12}$Al$_{12}$O$_{48}$·27H$_2$O (Na$_{12}$-A),[7] were prepared by a modification of Charnell's methods,[13] in-

cluding a second crystallization using seed crystals from the first synthesis. Each of two single crystals (0.08 mm on an edge) was lodged in a fine glass capillary.

Crystals of Tl$_{3.4}$Zn$_{4.3}$–A and Tl$_{5.5}$Zn$_{3.25}$–A were prepared using exchange solutions in which mole ratios of TlNO$_3$ and Zn(NO$_3$)$_2$ were 1:50 and 1:1, respectively, with total concentration of 0.05 M.

The crystal was ion exchanged by flow methods-a continuous stream of fresh mixed solution of TlNO$_3$ and Zn(NO$_3$)$_2$ flowed past the crystal at a velocity of approximately 1.0 cm/sec for 5 days at 25(1) °C. Then each crystal was dehydrated at 450 °C and 2 × 10^{-6} Torr for 2 days. After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by a torch. Microscopic examination showed that both crystals had become dark brown color. Then the crystal was mounted on a goniometer head.

X-Ray Data Collection. The diffraction intensities were collected at 22(1) °C. The cubic space group *Pm3m* (no systematic absences) was used instead of *Fm3c* throughout this work for reasons discussed previously.[14-16] 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 radiation (Kα_1, λ = 0.70930 Å, Kα_2, λ = 0.71359 Å). In each case, the unit cell constants at 22(1) °C, as determined by least squares refinement of 25 intense reflections for which 17°<2θ<24° are a = 12.100(2) Å for Tl$_{3.4}$Zn$_{4.3}$–A and a = 12.092(2) Å for Tl$_{5.5}$Zn$_{3.25}$–A, respectively.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \le k \le l$ and lhk, $l \le h \le k$) were examined. The intensities were measured using ω -2θ san 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 speed, ranging between 0.132° and 0.344° in ω min^{-1}. 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 fluc-
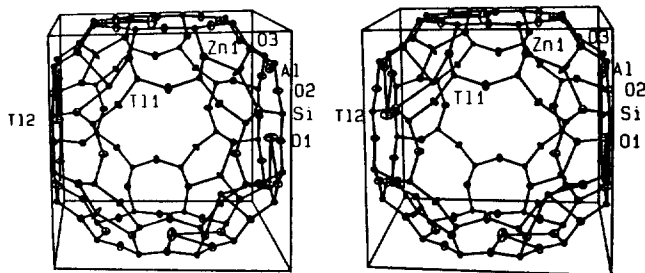
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Figure 1. A stereoview of the large cavity of dehydrated Tl$_{3.4}$Zn$_{4.3}$-A. Four Zn^{2+} ions at Zn(1), two Tl$^+$ ions at Tl(1), and two Tl$^+$ ions at Tl(2) are shown (see Table 4, a). About 70% of the large cavities have this arrangement. Ellipsoids of 20% probability are used.

tuations 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.

The intensities were corrected for Lorentz and polarization effects; the reduced intensities were merged and the resultant estimated standard deviation were assigned to each average reflection by the computer programs, PAINT and WEIGHT.[17] An absorption correction (μR ca. 0.3 for Tl$_{3.4}$Zn$_{4.3}$-A and μR ca. 0.5 for Tl$_{5.5}$Zn$_{3.25}$-A) was judged to be negligible and was not applied. All unique reflections for which $2\theta < 70°$ for crystals were examined by counter methods. Only those for which $I > 3\sigma(I)$ were used for structure solution and refinement. These amounted to 236 of the 881 reflections examined for the dehydrated Tl$_{3.4}$Zn$_{4.3}$-A,

and 202 of the 881 reflections for the dehydrated Tl$_{5.5}$Zn$_{3.25}$-A, respectively.

Structure Determination

All structure calculations were done using the Structure Determination Package (SDP)[17] programs supplied by Enraf-Nonius. The computer program used for least-square refinement minimizes the quantity $\Sigma w(F_o - |F_c|)^2$ were w is the weight of an observation, which is the reciprocal square of its estimated standard deviation, σ (F_o). Atomic scattering factors[18] for Tl$^+$, Zn^{2+}, O$^-$, and (Si, Al)$^{1.75+}$ (the average of Si^0, Si^{4+}, Al^0, and Al^{3+}), all properly modified to include the real components ($\Delta f'$) of the anomalous dispersion corrections,[19,20] were used throughout the refinements.

(a) Dehydration Tl$_{3.4}$Zn$_{4.3}$-A. Initial full-matrix, least-squares refinement of the structure was carried out using the aluminosilicate framework [(Si, Al), O(1), O(2), and O(3)] (see Figure 1 for the identities of the atoms) atomic coordinates of dehydrated Ag$_7$Tl$_5$-A[21] and two 6-ring Tl$^+$ ions at (0.25, 0.25, 0.25). The occupancy of Tl$^+$ ions at Tl(1) refined 1.6(1) (see Table 1). This model converged at R_1 = 0.386 and R_2 = 0.469. A difference Fourier map revealed two large peaks at (0.0, 0.458, 0.458) and (0.193, 0.193, 0.193) with heights of 5.37(27) eÅ^{-3} and 7.67(33) eÅ^{-3}, respectively. The first peak was assigned to Tl$^+$ ions, and the second was to Zn^{2+} ions.

Since ionic radii of Zn^{2+} and Tl$^+$ ions are quite different, Zn^{2+} = 0.74Å vs. Tl$^+$ = 1.47Å, and their atomic scattering factors are also different, 28 e$^-$ for Zn^{2+} vs. 80 e$^-$ for Tl$^+$, it is

Table 1. Positional, Thermal,[a] and Occupancy Parameters of Dehydrated Tl$_{12-2x}$Zn$_x$-A(x = 4.3 and 3.25)

(1) Dehydrated Tl$_{3.4}$Zn$_{4.3}$-A

Atom	Wyc. Pos.	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[b]Occupancy varied	fixed
(Si, Al)	24(k)	0	1833(3)	3679(3)	20(2)	16(20)	11(2)	0	0	4(4)		[c]24.0
O(1)	12(h)	0	2010(2)	5000	120(20)	110(20)	30(10)	0	0	4		12.0
O(2)	12(i)	0	3025(7)	3025(7)	19(8)	27(5)	27(5)	0	0	-20(20)		12.0
O(3)	24(m)	1139(5)	1139(5)	3247(8)	59(5)	59(5)	72(8)	50(20)	-70(10)	-70(10)		24.0
Tl(1)	8(g)	2251(2)	2251(2)	2251(2)	29(1)	29(1)	29(1)	1(5)	1(5)	1(5)	1.56(4)	1.60
Zn(1)	8(g)	1866(5)	1866(5)	1866(5)	89(2)	89(2)	89(2)	152(5)	152(5)	152(5)	4.18(16)	4.30
Tl(2)	12(i)	0	4610(4)	4610(4)	190(10)	103(5)	103(5)	0	0	-110(10)	1.75(6)	1.80

(b) Dehydrated Tl$_{5.5}$Zn$_{3.25}$-A

Atom	Wyc. Pos.	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	[b]Occupancy varied	fixed
(Si, Al)	24(k)	0	1828(4)	3679(3)	21(2)	21(3)	20(2)	0	0	-2(6)		[c]24.0
O(1)	12(h)	0	2060(2)	5000	110(20)	80(20)	60(10)	0	0	0		12.0
O(2)	12(i)	0	3037(8)	3037(8)	30(10)	34(7)	34(7)	0	0	-10(20)		12.0
O(3)	24(m)	1150(6)	1150(6)	3244(9)	67(6)	67(6)	70(10)	40(20)	-60(10)	-60(10)		24.0
Tl(1)	8(g)	2584(2)	2584(2)	2584(2)	34(1)	34(1)	34(1)	-6(3)	-6(3)	-6(3)	2.61(5)	2.50
Zn(1)	8(g)	1863(9)	1863(9)	1863(9)	198(40)	198(40)	198(40)	384(9)	384(9)	384(9)	3.54(17)	3.25
Tl(2)	12(i)	0	4579(3)	4579(3)	270(10)	128(5)	128(5)	0	0	-160(10)	2.49(6)	2.50
Tl(3)	8(g)	1040(20)	1040(20)	1040(20)	110(10)	110(10)	110(10)	90(30)	140(0)	145(0)	0.43(6)	0.50

[a]Positional and isotropic 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. The anisotropic temperature factor = exp[-(β_{11}h^2 + β_{22}k^2 + β_{33}l^2 + β_{12}hk + β_{13}hl + β_{23}kl)]. [b]Occupancy factors are given as the number of atoms or ions per unit cell. [c]Occupancy for (Si) = 12; occupancy for (Al) = 12.

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

Interatom	$Tl_{3.4}Zn_{4.3}$-A	$Tl_{5.5}Zn_{3.25}$-A
(Si, Al)–O(1)	1.612(5)	1.623(5)
(Si, Al)–O(2)	1.645(8)	1.656(6)
(Si, Al)–O(3)	1.697(5)	1.698(5)
Tl(1)–O(3)	2.558(5)	2.578(6)
Tl(2)–O(1)	3.19(2)	3.08(2)
Tl(2)–O(2)	2.71(1)	2.64(2)
Zn(1)–O(3)	2.08(1)	2.07(1)
Tl(3)–O(3)		2.67(2)
O(1)–(Si,Al)–O(2)	111.3(7)	107.9(6)
O(1)–(Si,Al)–O(3)	111.8(5)	112.9(5)
O(2)–(Si,Al)–O(3)	106.7(2)	106.3(3)
O(3)–(Si,Al)–O(3)	108.6(3)	110.0(4)
(Si,Al)–O(1)–(Si,Al)	165(1)	160(1)
(Si,Al)–O(2)–(Si,Al)	147.5(4)	145.9(5)
(Si,Al)–O(3)–(Si,Al)	135.2(5)	134.0(6)
O(3)–Zn(1)–O(3)	119.9(3)	120.0(3)
O(3)–Tl(1)–O(3)	89.6(2)	87.9(2)
O(1)–Tl(2)–O(2)	53.5(1)	54.6(2)
O(3)–Tl(3)–O(3)		84.3(1)

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

Table 3. Deviation of Atoms(Å) from the (111) Plane at O(3)

Atom	$Tl_{3.4}Zn_{4.3}$-A	$Tl_{5.5}Zn_{3.25}$-A
O(2)	0.367(5)	0.370(6)
Zn(1)	0.052(3)	0.031(7)
Tl(1)	1.486(2)	1.542(1)
Tl(3)		-1.687(11)

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

easy to distinguish Zn^{2+} from Tl^+ ions. Simultaneous occupancy, positional, and anisotropic thermal paramater refinement of all positions, converged to the error indices $R_1 = 0.075$ and $R_2 = 0.073$. Finally, the occupancies of Zn(1), Tl(1), Tl(2) ions per unit cell were fixed at the values shown in Table 1 as all other parameters were refined to convergence. The final R values were $R_1 = 0.075$ and $R_2 = 0.075$.

(b) Dehydrated $Tl_{5.5}Zn_{3.35}$-A. Full matrix least-squares refinement of the structure was commenced using the atomic parameters studied from the previous crystal of $Tl_{3.4}Zn_{4.3}$-A. Anisotropic refinement of framework atoms converged to $R_1 = 0.527$ and $R_2 = 0.638$. An examination of a difference Fourier map indicated three large peaks; two threefold axes peaks, one nearly on the 6-ring plane[12] at (0.190, 0.190, 0.190) and the other deep into the large cavity at (0.258, 0.258, 0.258), and the third the 8-oxygen plane at (0.0, 0.46, 0.46). All three peaks were stable in least-squares refinement. The first peak was refined as 3.25 Zn^{2+} ions. The second and third peak were refined as 2.61 Tl^+ ions and 2.49 Tl^+ ions, respectively (see Table 1). This model converged at R_1 to 0.146 and R_2 to 0.159. Anisotropic refinement of all atoms converged quickly to the error indices, $R_1 = 0.070$ and $R_2 = 0.064$. From successive difference Fourier map, one

peak was revealed at (0.11, 0.11, 0.11) of height 3.57(25) $eÅ^{-3}$. Including this cation position as 0.5 Tl^+ ion at Tl(3), anisotropic refinement converged with $R_1 = 0.062$ and $R_2 = 0.054$. Fixing the occupancies at values shown in Table 2 converged to $R_1 = 0.064$ and $R_2 = 0.057$. All shifts in the final cycles of least-squares were less than 0.5% of their corresponding esd's.

The final structure parameters are presented in Table 1, Interatomic distances and angles are given in Table 2.

Discussion

(a) Dehydrated $Tl_{3.4}Zn_{4.3}$-A. In crystal structure of dehydrated $Tl_{3.4}Zn_{4.3}$-A, 1.6 Tl^+ ions at Tl(1) are located on threefold axes and recessed 1.486(2) Å into large cavity from (111) plane at O(3) (see Table 3). These positions have been also found in previous works.[21,22] Each of these Tl^+ ions is coordinated to three O(3) oxygens at 2.558(5) Å. As compared to the sum of Tl^+ and O^{2-} radii, 2.79 Å,[23] these bonds are short and therefore a little bit covalent.

1.8 Tl^+ ions at Tl(2) are associated with 8-ring oxygens and located in the plane of the 8-oxygen ring, but not at their centers. They approach to two framework O(1) oxygens and one O(2) oxygen at 3.19(2) Å and 2.71(1) Å, respectively. These distances are very similar to those of previous structures.[21,22]

4.3 Zn^{2+} ions at Zn(1) are located only 0.052(3) Å away from (111) plane at O(3) and are coordinated to three O(3)'s with Zn(1)–O(3) distance of 2.08(1)Å. The O(3)–Zn(1)–O(3) angle of 119.9(3)° indicates that Zn(1) has achieved trigonal-planar coordination (see Table 2).

The fractional occupancies observed at Zn^{2+} ions and Tl^+ ions in the structure of $Tl_{3.4}Zn_{4.3}$-A indicate that at least three different kinds of unit cells exist. About 70% of unit cell may have 4 Zn^{2+} ions at Zn(1), 2 Tl^+ ions at Tl(1) and 2 Tl^+ ions at Tl(2). About 20% of unit cell may consist of 5 Zn^{2+} ions at Zn(1) and 2 Tl^+ ions at Tl(2) (see Table 4). Remaining 10% may consist of 5 Zn^{2+} ions at Zn(1), one Tl^+ ion at Tl(1) and one Tl^+ ion at Tl(2).

Zn^{2+} ions have been arranged in a tetrahedral fashion in Figure 1 among their low-occupancy equipoints in order to maximize their intercationic distances: Zn(1)–Zn(1) = 6.38 Å.

(b) Dehydrated $Tl_{5.5}Zn_{3.25}$-A. 3.25 Zn^{2+} ions at Zn(1), 2.50 Tl^+ ions at Tl(1) and 2.50 Tl^+ ions at Tl(2) are in the very similar positions to those of the dehydrated $Tl_{3.4}Zn_{4.3}$-A.

3.25 Zn^{2+} ions at Zn(1), 2.50 Tl^+ ions at Tl(1) and 0.5 Tl^+ ion at Tl(3) are distributed on the three different 6-ring sites. Zn^{2+} ions occupy almost the center of the 6-oxygen rings (Table 2) and the sites of near trigonal planar coordination. Tl^+ ions at Tl(1) occupy threefold axis position near 6-ring, recessed 1.542(1) Å into the large cavity from the (111) plane at O(3) (Table 3). Tl^+ ion at Tl(3) lies relatively far inside of the sodalite cavity. *ca.* 1.687(11) Å from (111) plane of O(3)'s. The distance between Tl(3) and its nearest framework oxygen at O(3) is 2.67(2) Å.

2.5 Tl^+ ions at Tl(2) are associated with 8-ring oxygens and located in the plane of the 8-oxygens. These Tl^+ ions at Tl(2) are coordinated to two O(1) framework oxygen at 2.64 Å.

About 25% of unit cell may have a configuration shown in Figure 2 (see Table 4). A plausible arrangement of the
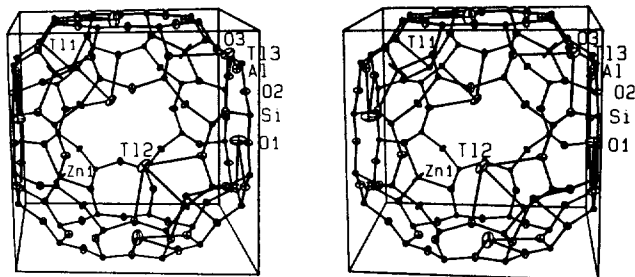
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Figure 2. A stereoview of the large cavity of dehydrated $Tl_{5.5}Zn_{3.25}$-A. Three Zn^{2+} ions at Zn(1), two Tl^+ ions at T1(1), three Tl^+ ion at Tl(2), and Tl^+ ion at Tl(3) are shown (see Table 4, b). About 25% of the large cavities have this arrangement. Ellipsoids of 20% probability are used.

Table 4. Possible Unit Cell Compositions of Dehydrated $Tl_{12-2x}Zn_x$-A (x = 4.3 and 3.25)

(a) Dehydrated $Tl_3Zn_{4.3}$-A

Atom	70%	10%	20%
Zn(1)	4	5	5
Tl(1)	2	0	1
Tl(2)	2	2	1

(b) Dehydrated $Tl_{5.5}Zn_{3.25}$-A

Atom	25%	25%	25%	25%
Zn(1)	4	3	3	3
Tl(1)	2	3	3	2
Tl(2)	2	3	2	3
Tl(3)	0	0	1	1

nine cations is presented (see Table 1 and 4, Figure 2). The 6-ring cations have been placed within their partially occupied equipoints so as to maximize the distribution of positive charge (to balance most evenly the anionic charge of the framework) and to minimize their electrostatic repulsions (to maximize the shorter of interactionic approaches). To minimize electrostatic repulsion three Zn^{2+} ions at Zn(1) are placed in a triangular fashion. Two Tl^+ ions at Tl(1) are placed at opposite sides deep into the large cavity. Three Tl^+ ions at Tl(2) are filled all 8-ring sites. One Tl^+ ion at Tl(3) is located inside of the sodalite cavity.

Tl^+ ions (ionic radius = 1.47 Å) at Tl(2) lie off the center of 8-rings, while Rb^+ ions (ionic radius = 1.47 Å) in dehydrated Ag_9Rb_3-A[24] lie at the center of 8-rings. Thus the approaching distance of Tl^+ to O(2) of eight oxygen (2.71 Å for $Tl_{3.4}Zn_{4.3}$-A and 2.64 Å for $Tl_{5.5}Zn_{3.25}$-A) is shorter than that of Rb^+ ion to framework oxygen (ca. 3.54 Å). This result indicates that Tl^+ ions have larger covalent characters than Rb^+ ions.

The crystal structure of Zn_5K_2-A,[11] evacuated at 400 °C was studied by Seff and Raghavan. In this structure five Zn^{2+} ions per unit cell occupy three nonequivalent position, all on the unit cell threefold axes. Of these ions, 1.5 Zn^{2+} ions lie very close to their 6-ring plane and have trigonal planar coordinations and the remaining 3.5 ions are either recessed into sodalite unit or into the large cavity. Each of these 3.5 Zn^{2+}

ions is associated with one water molecules or hydroxide ion, which is recessed further into the corresponding cavity to complete and approximate tetrahedral coordination sphere. In the present study, angles of O(3)-Zn(1)-O(3) for both structures are *ca.* 120.0°, ideal trigonal planar angles and also no water molecule is associated with Zn^{2+} ions. This indicate that the crystals studies in present work are fully dehydrated.

In the crystal structures of $Tl_{3.4}Zn_{4.3}$-A and $Tl_{5.5}Zn_{3.25}$-A, totals of 5.9 and 6.25 cations, respectively, per unit cell occupy the 6-ring sites. Smaller Zn^{2+} ions occupy only the 6-ring site, and larger Tl^+ ion occupy deep into large cavity and also sodalite unit associated with 6-ring oxygen. This indicates that Tl^+ ions do not have any preference to a particular site. 1.6 Tl^+ ions for $Tl_{3.4}Zn_{4.3}$-A ad 2.5 Tl^+ ions for $Tl_{5.5}Zn_{3.25}$-A occupy the 8-ring sites despite of the presence and ready availability of vacant 6-ring sites. The present structures are similar to the structures of Zn_5K_2-A and Pb_6-A[25] which two K^+ ions and one Pb^{2+} ion, respectively, occupy the 8-ring sites.

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Synthesis and Biological Activities of the Alternating Copolymers Containing Cyclic Ether Rings along with Carboxyl or Hydroxyl Groups on Their Backbones

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The alternating copolymers of dihydropyran(DP)-maleic anhydride(MA), dihydrofuran(DF)-MA and DF-vinylene carbonate(VC) were prepared by free radical copolymerization of DP or DF with MA or VC. The reactivity ratios for poly(DF-VC) were found to be less than unity (0.05, 0.04) and its alternating sequences were obtained by feeding an equimolar amount of the comonomers at the onset of copolymerizations. The copolymers were hydrolyzed to give poly(TP-CE), poly(TF-CE) and poly(TF-HE), whose cytotoxicities against normal and tumor cells (3LL, B16) were measured *in vitro*.

Introduction

Several synthetic polymers are known to exhibit a broad range of biological activities against tumor, virus and fungi.[1-5] It was well documented that polymers with high density of carboxylic acid functionalities as hydrophilic groups along the polymer chain have exhibited high antitumor activities.[6] Recently we have demonstrated that the tetrahydropyran(THP) and/or tetrahydrofuran rings as hydrophobic groups on the polymer chain also play a significant role in the antitumor activity of the polymer.[7-9] It is therefore of interest whether the copolymers shown in Scheme 1, which are containing cyclic ether rings as hydrophobic groups together with carboxyl or hydroxyl as hydrophilic groups along the polymer chain, would exhibit the relevant biological activities.

In this paper we report the synthesis and biological activities of poly[(tetrahydropyran-2,3-diyl)(1,2-dicarboxyethylene)] [poly(TP-CE)], poly[(tetrahydrofuran-2,3-diyl)(1, 2-dicarboxyethylene)] [poly(TF-CE)] and poly[(tetrahydrofuran-2,3-diyl)(1,2-dihydroxyethylene)] [poly(TF-HE)]. The outline of syntheses for the alternating copolymers obtained by free radical copolymerizations are illustrated in Scheme 1.

Experimental

Purification of chemicals; 3,4-dihydro-2H-pyran (Bp: 86 °C), 2,3-dihydrofuran (Bp: 55 °C) and vinylene carbonate (Bp$_{15}$: 47 °C) were distilled before use. AIBN was recrystalized from methanol. Maleic anhydride (MA) was sublimed under vacuum. Acetone was refluxed over P$_2$O$_5$ and distilled
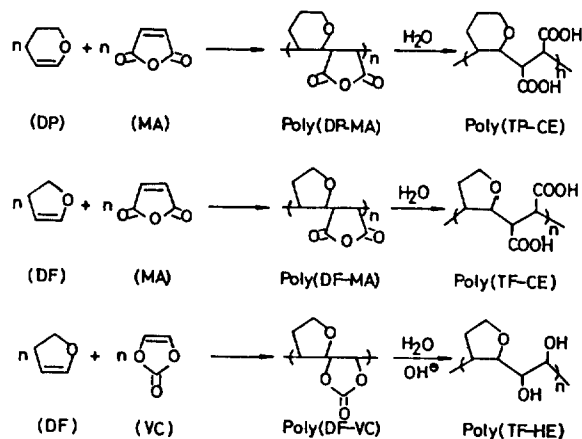
Scheme 1

under N$_2$ before use.

Copolymerization. Calculated amount of monomers, solvent and initiator (AIBN) were charged in the copolymerization tube, which were immersed in a Dewar flask containing dry ice and acetone. Following conventional freeze-thaw treatment under N$_2$, the tubes were sealed and placed in a temperature controlled bath for a fixed period of time. The solutions of poly(DP-MA) and poly(DF-MA) in acetone, and poly(DF-VC) in chloroform were precipitated in ether several times and dried in vacuo over P$_2$O$_5$ at 50 °C in a drying pistol.

Hydrolysis. poly(tetrahydropyran-2,3-diyl)(1,2-dicarboxyethylene)] [poly(TP-CE)] and poly[(tetrahydrofuran-2, 3-diyl)(1,2-dicarboxyethylene)] [poly(TF-CE)]. Aqueous solutions (25 ml) of poly(DP-MA) (1g) or poly(DF-MA) (1g)