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(24) We are grateful to a referee who pointed out that a second isomer of *trans*-$[Co([14]aneN_4)Cl_2]^+$ has been prepared by reaction with HCl of the $(+)_{546}$-*cis*-oxalato complex.[26] Referring to Figure 4, and replacing the uppermost three-carbon linkage with a two-carbon linkage, the possible trans isomers of $[14]aneN_4$ can be designated by structures b through f. Calculations for these isomers of *trans*-$[Co([14]aneN_4)Cl_2]^+$ result in total strain energy values of 11.53 (b), 27.78 (c), 19.51 (d), 20.47 (e), and 20.04 kcal (f), respectively. The isomer initially prepared by Bosnich et al.[7] is assigned the lowest energy structure (b) analogous to the known structure[27] of the $[Ni([14]aneN_4)Cl_2]$ complex. Structure d has been assigned to the isomer resulting from decomposition of the *cis*-oxalato complex.[26] It should be noted that *cis*-$[Co([14]aneN_4)Cl_2]^+$ has been shown by x-ray crystallography[28] to have N-H configurations corresponding to isomer d of the *trans*-dichloro derivative. For structures b and d we calculate ideal metal-nitrogen distances of 2.13 and 2.11 Å, respectively. Thus we would predict very similar values of Dq^{xy} for these two trans isomers, and indeed the observed spectra support this prediction.

(25) The M-N distances of Table XII are not expected to be accurate in the absolute sense; however, the differences between them are believed to have significance. Consequently, it is preferable to consider *ideal M-N* as a parameter reflecting the fit or nonfit of a given metal ion to the ring. Alternately, one could arbitrarily seek to add or subtract an increment that would bring this parameter into coincidence with experiment for the best fit case. We have chosen not to use this alternate procedure.

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Near-Zero-Coordinate Thallium(I). The Crystal Structures of Hydrated and Dehydrated Zeolite A Fully Exchanged with TlOH

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Abstract: The crystal structures of vacuum-dehydrated (a = 12.180 (2) Å) and hydrated (a = 12.380 (2) Å) zeolite A which had been fully exchanged with aqueous TlOH have been determined by single-crystal x-ray diffraction techniques in the cubic space group $Pm3m$. The structures were refined to final R (weighted) indices of 0.057 and 0.062, respectively. In the dehydrated structure, six equivalent Tl^+ ions lie on threefold axes in the large cavity opposite 6-oxygen rings, and three other Tl^+ ions occupy an equipoint in the planes of the oxygen 8-rings. In the sodalite unit, two equivalent Tl^+ ions are located on a common threefold axis near 6-rings on opposite sides of the origin. *The twelfth* Tl^+ *ion occupies a unique and unusual position in the large cavity, on a mirror plane and off a threefold axis, 3.21 Å from the nearest framework oxide ion. This* Tl^+ *ion is approximately 0.42 Å farther from its nearest neighbor than the sum of the ionic radii would indicate.* This situation has occurred because insufficient sites are available on the inner surface of the zeolite to accommodate all of the large cations present—by difference, one Tl^+ ion per unit cell must occupy a site where it can interact only weakly with the framework, its only possible ligand. In the hydrated structure, 13 Tl^+ ions are present. Seven occupy threefold axis sites opposite 6-rings in the large cavity, approximately 1.5 Å from the O(3) planes, while three Tl^+ ions are located in the planes of the 8-rings as in the dehydrated structure. In the sodalite unit, the remaining three Tl^+ ions form a nearly equilateral triangle, and are bridged, it is presumed, by a hydroxide ion which entered the zeolite from the TlOH exchange solution. Nine water molecules per unit cell have been located: three bridge between the Tl^+ ions opposite 6-rings in the large cavity, and the remaining six are associated with the three Tl^+ ions in the 8-oxygen rings.

Zero-coordinate cations,[1-4] or severely under-coordinated cations (this work), can be prepared by the ion-exchange of large monovalent cations into zeolite A followed by vacuum dehydration. Such unusual coordination occurs because all of the sites available to large cations at the zeolite framework are filled before all of the anionic charges of the framework are balanced, leaving some cations uncoordinated. Reference 2 discusses in some detail the conditions necessary for zero-coordinate cations to exist in zeolite A.

Three examples of zero-coordinate cations are known. In dehydrated K_{12}-A,[1,5] one K^+ ion per unit cell is located deep within the large cavity, 4.25 Å from its nearest neighbors, three oxide ions of a 6-oxygen ring.[6] In dehydrated $Rb_{11}Na_1$-A,[2,3,5] a Rb^+ ion occupies a similar position at distances of 4.35 Å. In dehydrated Cs_7K_5-A,[4,5] a K^+ ion is 4.40 Å from the same nearest neighbors. These monovalent cations can be considered zero-coordinate because their closest approaches to framework oxide ions are long, in comparison to the sum of the appropriate ionic radii, by 1.6-1.75 Å.[7]

This work was undertaken in the hope of preparing fully Tl^+-exchanged dehydrated zeolite A, which should contain an under-coordinate, possibly zero-coordinate, Tl^+ ion. This expectation was based on the previously determined structure of dehydrated $Rb_{11}Na_1$-A[2,3]—the ionic radius of Tl^+ (1.47 Å)[7] is the same as that of Rb^+. It was also suspected that dehydrated Tl_{12}-A might be different from dehydrated $Rb_{11}Na_1$-A[2,3] and K_{12}-A[1] because of the greater covalency of Tl^+.

The crystal structures of hydrated and dehydrated Tl^+-exchanged zeolite A have been studied before. In 1971, Riley, Seff, and Shoemaker determined the crystal structures of hydrated and dehydrated Tl_{11}-A;[8] more recently and less accurately, the hydrated structure was redetermined by Thöni[9] who was able to locate only ten Tl^+ ions per unit cell. The

Table I. Positional, Thermal,[a] and Occupancy Parameters for Tl_{12}-A

	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
a. Dehydrated											
(Si,Al)	24(k)	0	1824 (6)	3670 (5)	18 (4)	16 (4)	11 (4)	0	0	1 (7)	1[c]
O(1)	12(h)	0	2082 (20)	½	38 (21)	80 (24)	29 (18)	0	0	0	1
O(2)	12(i)	0	3028 (15)	3028 (15)	29 (18)	32 (12)	32 (12)	0	0	53 (31)	1
O(3)	24(m)	1145 (8)	1145 (8)	3256 (12)	22 (7)	22 (7)	40 (13)	−2 (18)	30 (15)	30 (15)	1
Tl(1)	8(g)	2589 (1)	2589 (1)	2589 (1)	29 (7)	29 (7)	29 (7)	−3 (2)	−3 (2)	−3 (2)	¾
Tl(2)	12(i)	0	4601 (6)	4601 (6)	181 (14)	152 (11)	152 (11)	0	0	−235 (23)	¼
Tl(3)	8(g)	1044 (5)	1044 (5)	1044 (5)	51 (3)	51 (3)	51 (3)	0(8)	0(8)	0(8)	¼
Tl(4)	24(m)	2587 (28)	3371 (54)	3371 (54)	0 (16)	338 (54)	338 (54)	20 (71)	20 (71)	22 (15)	1/24
b. Hydrated											
(Si,Al)	24(k)	0	1837 (5)	3724 (5)	15 (4)	2 (4)	5 (4)	0	0	−3 (6)	1[c]
O(1)	12(h)	0	2233 (16)	½	48 (19)	26 (16)	6 (13)	0	0	0	1
O(2)	12(i)	0	2932 (11)	2932 (11)	30 (16)	11 (10)	11 (10)	0	0	−31 (23)	1
O(3)	24(m)	1124 (9)	1124 (9)	3450 (13)	17 (7)	17 (7)	67 (15)	18 (18)	7 (16)	7 (16)	1
Tl(1)	8(g)	2607 (1)	2607 (1)	2607 (1)	45 (1)	45 (1)	45 (1)	14 (2)	14 (2)	14 (2)	⅞
Tl(2)	12(i)	0	4568 (5)	4568 (5)	211 (14)	127 (8)	127 (8)	0	0	−189 (17)	¼
Tl(3)	8(g)	1189 (22)	1189 (22)	1189 (22)	171 (19)	171 (19)	171 (19)	120 (50)	120 (50)	120 (50)	⅛
Tl(4)	48(n)	228 (18)	845 (14)	1255 (16)	3.7 (6)[d]						1/24
O(4)	24(l)	1852 (51)	3513 (49)	½	1.2 (1.2)[d]						¼
O(5)	12(j)	2642 (54)	2642 (54)	½	2 (2)[d]						¼

[a] Positional and anisotropic thermal parameters are given × 10^4. Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. See Figures 1 and 3 for the identities of the atoms. The anisotropic temperature factor = $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Rms displacements can be calculated from β_{ii} values using the formula, $\mu_i = 0.225a(\beta_{ii})^{1/2}$. [c] Occupancy for (Si) = ½; occupancy for (Al) = ½. [d] Isotropic thermal parameter in units of Å^2.

crystal structure of hydrated fully Tl^+-exchanged zeolite A was also determined (1) to verify the cation composition deduced from the dehydrated structure, (2) to learn the effect of the twelfth Tl^+ ion on the positions of the other cations as compared to Tl_{11}-A,[8] and (3) to check the structure[9] determined by Thöni, specifically concerning the location of water molecules. This work is judged to be considerably more accurate than the previous studies of Tl^+-exchanged zeolite A because crystals approximately six times larger by volume were used, resulting in substantially larger data sets.

Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's methods,[10] including a second crystallization using seed crystals from the first synthesis. A single crystal 0.10 mm on an edge was lodged in a fine glass capillary. The exchange was then performed using flow methods; 0.1 M aqueous TlOH was allowed to flow past the crystal at a velocity of approximately 1.0 cm/s. This procedure was conducted at 25 (1) °C for 5 days. The crystal was then dehydrated for a period of 48 h at 350 °C and 5 × 10^{-6} Torr. After cooling to room temperature, the crystal, still under vacuum, was sealed in its capillary by torch. Microscopic examination showed that the crystal was dark gray to black in color. The hydrated crystal (0.09 mm on an edge) used in this study was prepared by the same exchange procedure and remained clear. Subsequent diffraction intensities for both crystals were collected at 23 (1) °C.

An x-ray fluorescence analysis for thallium was performed on the same single crystal of hydrated Tl^+-exchanged zeolite A from which x-ray diffraction data were collected. Thallium M and L lines were observed at 20 keV and 50 keV per channel using a Cambridge Stereoscan S410-B electron microscope with an x-ray fluorescence analyzer. A finely ground mixture (61.5% Tl) of ultrapure $TlNO_3$ and hydrated Na_{12}-A was used as a standard. Although the results indicated the presence of 13 Tl^+ ions per unit cell (61.5% Tl), the precision was not high enough to eliminate the compositions Tl_{12}-A (59.5% Tl) and Tl_{14}-A (63.2% Tl). Thirteen water molecules were assumed to be present per unit cell in these calculations. This result corroborates the more precise crystallographic determination of 13 Tl^+ ions per unit cell (see Structure Determination section).

The cubic space group $Pm3m$ (no systematic absences) appeared to be appropriate.[6a,11-13] A Syntex four-circle computer-controlled diffractometer with a graphite monochromator and a pulse-height analyzer was used throughout for preliminary experiments and for the collection of diffraction intensities. Molybdenum radiation (Kα_1, λ 0.709 30 Å; Kα_2, λ 0.713 59 Å) was used throughout. In each case, the cell constant, a = 12.180 (2) Å for the dehydrated crystal and a = 12.380 (2) Å for the hydrated crystal, was determined by a least-squares treatment of 15 intense reflections for which $2\theta < 24°$.

For each crystal, reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \leq k \leq l$, and lhk, $l \leq h \leq k$) were examined using the θ-2θ scan technique. Each reflection was scanned at a constant rate of 1.0 deg min^{-1} from 1° (in 2θ) below the calculated Kα_1 peak to 1° above the Kα_2 maximum; for the hydrated crystal, shorter ranges of 0.8° (in 2θ) were used. Background intensity was counted at each end of a scan range for a time equal to half the scan time. The intensities of three reflections in diverse regions of reciprocal space were recorded after every 100 reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection. All unique reciprocal lattice points (863 and 900 for the dehydrated and hydrated crystals, respectively) for which $4° < 2\theta < 70°$ were examined. The high upper limit for 2θ was chosen to give a more complete data set, even though few reflections with large 2θ values showed significant intensity.

The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization assuming the monochromator crystal to be half mosaic and half perfect in character; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.[14] The mean intensity for a reflection was calculated as $I = (I_{hkl} + I_{lhk})/2$, where $I_{hkl} = [\mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)](\omega)$, CT is the total integrated count obtained in a scan time t_c, B_1 and B_2 are the background counts each measured in time t_b, and ω is the scan rate. The standard deviation of I is

$$\sigma(I) = (\sigma^2(I_{hkl}) + \sigma^2(I_{lhk}))^{1/2}/2$$

and the standard deviation of each unmerged reflection is

$$\sigma(I_{hkl}) = [(\mathrm{CT} + B_1 + B_2)\omega^2 + (pI_{hkl})^2]^{1/2}$$

The value of p was taken as 0.02,[15] a value found to be appropriate for the instrumentation used. No absorption correction was applied to the data.

Only those reflections in each merged data set for which the net count exceeded three times its corresponding esd were used in structure

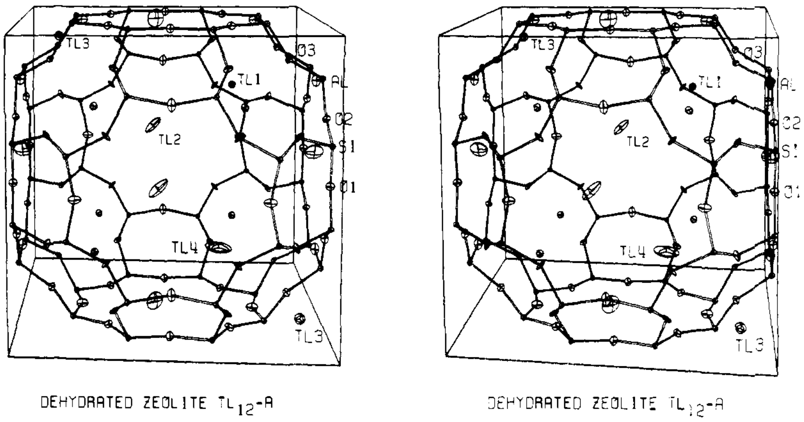

Figure 1. A stereoview[14] of dehydrated Tl_{12}-A. Ellipsoids of 20% probability are shown. The β_{11} thermal parameter on Tl(4) was increased by 1.0σ to produce a positive-definite thermal ellipsoid.

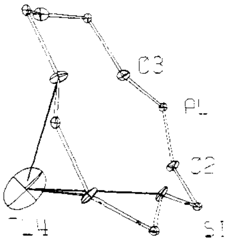

Figure 2. The coordination environment of Tl(4) in dehydrated Tl_{12}-A is shown.[14] Other comments in the caption to Figure 1 apply here as well. Bonds to two O(3)'s at 3.23 Å and to one O(2) at 3.21 Å are indicated.

solution and refinement. This amounted to 312 unique reflections for the dehydrated crystal and 321 for the hydrated crystal. For the hydrated crystal, the two low angle reflections (011) and (111) were removed because their peak profiles were very broad. The crystals have unit cell compositions of $Tl_{13}Si_{12}Al_{12}O_{48}{\cdot}9H_2O$ (a hydroxide ion and additional water molecules may be present) and $Tl_{12}Si_{12}Al_{12}O_{48}$ and will be subsequently referred to as Tl_{13}-A and Tl_{12}-A, respectively.

Structure Determination

Dehydrated Tl_{12}-A. Full-matrix least-squares refinement of dehydrated Tl_{12}-A began using the Tl^+ coordinates and framework positions of dehydrated Tl_{11}-A.[8] This initial model consisted of three Tl^+ ions (at Tl(2)) in the 8-oxygen rings, seven Tl^+ ions (at Tl(1)) opposite 6-rings in the large cavity, and one Tl^+ ion (at Tl(3)) opposite a 6-ring in the sodalite unit. Anisotropic refinement of the framework atoms and isotropic refinement of the Tl^+ positions converged to an R_1 index, $(\Sigma|F_o - |F_c||)/\Sigma F_o$, of 0.141 and a weighted R_2 index, $(\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2)^{1/2}$, of 0.124. A subsequent difference Fourier function revealed a peak of approximately 9.0 e $Å^{-3}$ at (0.10, 0.10, 0.10) indicating that the Tl(3) position contained an additional Tl^+ ion. Occupancy refinement of positions Tl(3) and T(1) clearly indicated the presence of two and six Tl^+ ions, respectively. The occupancy of Tl(2) remained three ions per unit cell as in Tl_{11}-A.[8] Anisotropic refinement of framework and all Tl^+ positions converged at R_1 and R_2 indices of 0.093 and 0.075, respectively. A difference Fourier function based on this 11 cation model revealed a peak of approximately 3.0 e $Å^{-3}$ at (0.25, 0.32, 0.32). This position, suspected of being the twelfth Tl^+ ion, at Tl(4), was stable in least-squares refinement and lowered the fractional error indices by nearly 0.02. Anisotropic refinement of this 12 Tl^+ model converged with the final error indices, $R_1 = 0.079$ and $R_2 = 0.057$. The goodness-of-fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 2.59; m (312) is the number of observations, and s (37) is the number of variables in least squares. All shifts in the final cycle of refinement were less than 0.2% of their corresponding esd's.

For dehydrated Tl_{12}-A, the largest peak on the final difference Fourier function, whose estimated standard deviation is 0.25 e $Å^{-3}$, was 2.9 e $Å^{-3}$ in height and was located just at Tl(1).

The final structural parameters are presented in Table Ia. Interatomic distances and angles are given in Table IIa. A listing of observed and calculated structure factors is available; see the paragraph at the end of this paper regarding supplementary material. A likely atomic arrangement in a particular unit cell is shown in Figure 1. It is consistent with the disordered structural model which has emerged from the crystallographic calculations. The unusual environment of Tl(4) is shown in Figure 2.

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

	a. Dehydrated Tl_{12}-A		
(Si,Al)-O(1)	1.650 (8)	O(1)-(Si,Al)-O(2)	107.1 (12)
(Si,Al)-O(2)	1.662 (10)	O(1)-(Si,Al)-O(3)	112.6 (9)
(Si,Al)-O(3)	1.698 (6)	O(2)-(Si,Al)-O(3)	106.9 (6)
Tl(1)-O(3)	2.617 (14)	O(3)-(Si,Al)-O(3)	110.5 (10)
Tl(1)-O(2)	3.243 (6)	(Si,Al)-O(1)-(Si,Al)	158.1 (10)
Tl(2)-O(1)	3.11 (2)	(Si,Al)-O(2)-(Si,Al)	146.1 (17)
Tl(2)-O(2)	2.71 (3)	(Si,Al)-O(3)-(Si,Al)	135.4 (10)
Tl(3)-O(3)	2.699 (16)	O(3)-Tl(1)-O(3)	88.0 (6)
Tl(3)-O(2)	3.64 (2)	O(3)-Tl(3)-O(3)	84.7 (4)
Tl(4)-O(3)	3.23 (6)	O(2)-Tl(4)-O(3)	91.4 (8)
Tl(4)-O(2)	3.21 (4)	O(3)-Tl(4)-O(3)	68 (2)
Tl(4)-Tl(3)	4.43 (9)	O(2)-Tl(1)-O(2)	107.0 (9)
Tl(3)-Tl(3)	4.405 (13)	O(2)-Tl(3)-O(2)	91.3 (6)
		O(1)-Tl(2)-O(1)	108.0 (2)
		O(2)-Tl(2)-O(2)	101.4 (2)
		O(1)-Tl(2)-O(2)	54.0 (2)
	b. Hydrated Tl_{13}-A		
(Si,Al)-O(1)	1.654 (8)	O(1)-(Si.Al)-O(2)	108.7 (10)
(Si,Al)-O(2)	1.672 (8)	O(1)-(Si,Al)-O(3)	110.4 (7)
(Si,Al)-O(3)	1.682 (6)	O(2)-(Si,Al)-O(3)	107.9 (6)
Tl(1)-O(3)	2.800 (15)	O(3)-(Si,Al)-O(3)	111.5 (11)
Tl(3)-O(3)	2.80 (3)	(Si,Al)-O(1)-(Si,Al)	145.6 (14)
Tl(2)-O(1)	2.940 (20)	(Si,Al)-O(2)-(Si,Al)	161.8 (13)
Tl(2)-O(2)	2.866 (21)	(Si,Al)-O(3)-(Si,Al)	145.9 (11)
Tl(4)-O(3)	2.95 (2)	O(3)-Tl(1)-O(3)	93.3 (5)
Tl(2)-O(4)	2.69 (6)	O(3)-Tl(3)-O(3)	93.3 (10)
Tl(1)-O(5)	2.963 (2)	O(1)-Tl(2)-O(1)	110.9 (2)
O(4)-O(1)	2.79 (6)	O(1)-Tl(2)-O(2)	55.5 (2)
Tl(4)-Tl(3)	3.52 (4)	O(1)-Tl(2)-O(4)	59.1 (4)
Tl(4)-Tl(4)	3.68 (4)	O(2)-Tl(2)-O(4)	78.3 (14)
Tl(4)-Tl(1)[b]	4.029 (20)	O(4)-Tl(2)-O(4)[b]	117 (2)
		Tl(1)-O(5)-Tl(1)	177.6 (15)
		O(3)-Tl(1)-O(5)	69.3 (6)

[a] The numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter. [b] These atoms are located in adjacent unit cells.

Hydrated Tl_{13}-A. Initial full-matrix least-squares refinement of the framework and Tl^+ parameters derived from Tl_{11}-A[8] converged to error indices, $R_1 = 0.143$ and $R_2 = 0.161$. This initial refinement used anisotropic thermal parameters for the framework and the principal thallium positions, Tl(1) and Tl(2). Simultaneous refinement of occupancy and thermal parameters of all Tl^+ ions quickly converged and indicated 7.1 Tl(1)'s, 2.8 Tl(2)'s, and 1.1 Tl(3)'s. These oc-

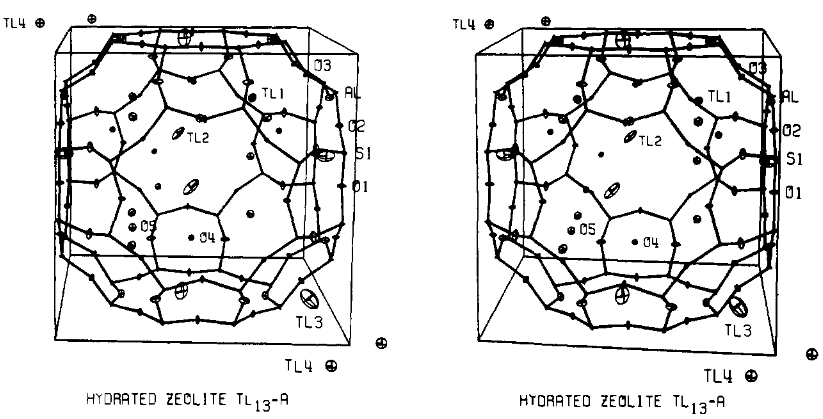

Figure 3. A stereoview[14] of hydrated Tl_{13}-A. Ellipsoids of 20% probability are shown. The β_{23} thermal parameter on O(2) was increased by 0.5σ to give a positive-definite thermal ellipsoid.

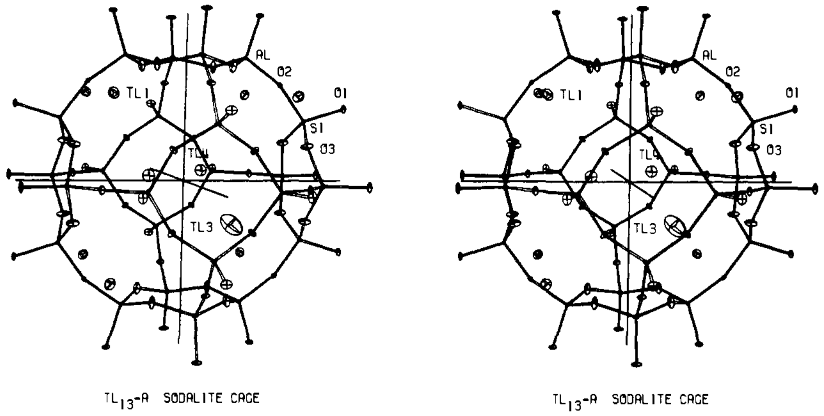

Figure 4. A stereoview[14] of the hydrated Tl_{13}-A sodalite unit. Other comments in the caption to Figure 3 apply here as well.

Table III. Deviations of Atoms (Å) from the (111) Plane at O(3)[a]

Dehydrated Tl_{12}-A		Hydrated Tl_{13}-A	
Tl(1)	1.56	Tl(1)	1.48
Tl(3)	−1.69[b]	Tl(3)	−1.55
Tl(4)	2.66[b]	Tl(4)	−2.45
Tl(2)	3.69		

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin. [b] These ions are on or near the same threefold axis.

cupancies were then fixed at 7, 3, and 1, respectively, per unit cell. A subsequent difference electron density function indicated a peak 5.6 e Å^{-3} in height at (0.01, 0.10, 0.11). Simultaneous occupancy and thermal parameter refinement converged at 1.85 ions at this position, Tl(4), indicative of two Tl^+ ions. The R_1 and R_2 indices were lowered by approximately 0.04 by the inclusion of the Tl(4) position.

A difference electron density function was then obtained which indicated three possible water positions, two of which refined by least squares. A position at (x, x, z) where $x = 0.26$ and $z = \frac{1}{2}$, indicative of bridging water molecules between Tl(1) ions, refined to an occupancy of three per unit cell. The other water position at $(x, y, \frac{1}{2})$, associated with the 8-oxygen rings and Tl(2), refined to an occupancy of six per unit cell, consistent with two water molecules per Tl(2). Anisotropic refinement of this 13 Tl^+ ion model was successful (converged to physically acceptable values) for all positions except Tl(4), O(4), and O(5), which were refined isotropically.

The error indices for the final model are $R_1 = 0.083$ and $R_2 = 0.062$. Lowering the occupancy of position Tl(4) from 2 to 1 to give a 12 Tl^+ ion model raised the error indices to 0.091 and 0.069 and resulted in a near-zero thermal parameter for that position. Also, refinement of position Tl(3) as six water molecules (an estimate of the maximum number that could exist at that equipoint with two ions at Tl(4)), followed by a difference electron density function, revealed a peak 2.7 e Å^{-3} in height near the Tl(3) position. This indicates that the density at Tl(3) cannot be attributed to water molecules. Furthermore, occupancy refinement of the Tl(3) position using O^- form factors converged at ten water molecules per unit cell, an unacceptably large number.

The goodness-of-fit is 3.04; the number of observations is 321; the number of parameters is 38. All shifts in the final cycle of least-squares refinement were less than 0.2% of their respective standard deviations. The largest maximum on the final difference electron density function, whose estimated standard deviation was 0.256 e Å^{-3}, was 3.3 e Å^{-3} in height and very near Tl(1). The final structural parameters are presented in Table Ib. Interatomic distances and angles are given in Table IIb. See the paragraph at the end of this paper regarding supplementary material. A likely atomic arrangement in a particular unit cell, consistent with the disordered structural model, is shown in Figures 3 and 4.

The full-matrix least-squares program used[14] in all structure determinations minimized $\Sigma w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of σ, its standard deviation. Atomic scattering factors[16,17] for Tl^+, 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. The scattering factors for Tl^+ and $(Si,Al)^{1.75+}$ were modified to account for the real component ($\Delta f'$) of the anomalous dispersion correction.[18,19]

Discussion

In the hydrated structure (see Tables Ib, IIb, and III, and Figures 3 and 4), the positions of the principal Tl^+ ions, Tl(1) and Tl(3), are nearly the same as those in previous investigations.[8,9] However, Tl_{13}-A contains three Tl^+ ions in the sodalite unit as compared to one in hydrated Tl_{11}-A.[8] In the large cavity, seven equivalent Tl^+ ions at Tl(1) occupy threefold axis positions opposite 6-oxygen rings, 1.48 Å from the [111] plane at O(3). Three Tl^+ ions per unit cell at Tl(2) are located in the plane of the 8-rings, but off their centers; this position is almost identical with the corresponding one in dehydrated Tl_{12}-A.

In the sodalite unit, two equivalent ions at Tl(4) are located at general positions, each 2.45 Å from an O(3) plane, while the remaining ion, at Tl(3), is located on a threefold axis, 1.55 Å from an O(3) plane. These three ions have been arranged in a triangular fashion within their low occupancy equipoints to maximize their intercationic distances; Tl(3)-Tl(4) = 3.52 Å and Tl(4)-Tl(4) = 3.68 Å.

The Tl(1)-O(3), Tl(3)-O(3), and Tl(2)-O(3) distances at 2.80, 2.80, and 2.86 Å agree closely with the sum of the corresponding ionic radii,[7] 2.79 Å. The Tl(4)-O(3) distance is somewhat long at 2.95 Å, probably due to repulsion from Tl(1) on the large cavity side of the nearest 6-ring (see Figure 4); Tl(4)-Tl(1) = 4.03 Å.

A total of nine water molecules per unit cell have been located in the large cavity at two equipoints. Three water molecules at O(5) bridge linearly between Tl(1) ions; Tl(1)-O(5)-Tl(1) = 177.6°. Similar bridging water molecules have been found in the hydrated structures of K_{12}-A[1] and $Rb_{11}Na_1$-A.[3] The maximum number of water molecules at O(5) is three; O(4)-O(5) approaches less than 2.0 Å would result if this occupancy were increased.

The six O(4) water molecules are associated with the 8-rings and with the Tl^+ ions at Tl(2) in them. One water molecule is on each side of each 8-ring, 2.69 Å from an ion at Tl(2); each Tl(2) is, then, coordinated by two O(4) water molecules. In turn, each O(4) water molecule hydrogen bonds to a framework O(1) ion at 2.79 Å. The small isotropic thermal parameter associated with O(4) is consistent with its strong interactions. The O(4) position had been previously located by Thöni.[9]

It is unusual that this hydrated structure contains 13 Tl^+ ions, one more positive charge than can be balanced by the anionic zeolite framework. It has been suggested that an occluded molecule of $NaAlO_2$, present in the sodalite unit, accounts for the ability of 13 Tl^+ ions per unit to exchange into zeolite A.[20] However, many zeolite A crystal structures have been determined in this laboratory, and never has an AlO_2^- anion been located, although unassignable residual electron density in the sodalite unit has been a frequent, but not constant, result. It is the experience of many workers in this area that well-formed crystals of zeolite A do not contain occluded aluminate in their sodalite units.

It is proposed that one molecule of TlOH per unit cell entered the zeolite during the ion-exchange procedure. The hydroxide ion should be located in the sodalite unit where an unreasonable concentration of positive charge would otherwise exist. A plausible bridging position between two or three of the Tl^+ ions in the sodalite unit could not be refined successfully by least squares. Upon dehydration, the excess molecule of TlOH has apparently decomposed, and, at 350 °C, migrated out of the zeolite, leaving 12 cations per unit cell and a black coating of Tl_2O on the crystal. Because Tl_2O melts at approximately 300 °C, it should be sufficiently mobile to migrate out of the zeolite at 350 °C. Dehydrated Tl_{11}-A[8] is colorless.

The unit cell constant, 12.380 (2) Å, found for the hydrated TlOH-exchanged crystal, is unusually large. However, a similarly large cell constant, 12.39 (2) Å, is found for the sodium nitrate salt inclusion complex[21] of zeolite A. Perhaps the presence of electrolyte molecules in the sodalite unit is responsible for the large cell constant in both instances.

In the dehydrated structure (Tables Ia, IIa, III, and Figures 1 and 2), three Tl^+ ions at Tl(2) are located in the planes of the 8-oxygen rings, but not at their centers, so as to make favorable approaches to the framework; Tl(2)-O(1) = 3.11 Å, and Tl(2)-O(2) = 2.71 Å. Eight of the remaining nine Tl^+ ions are distributed over two nonequivalent threefold axis equipoints. Six, at Tl(1), extend 1.56 Å into the large cavity from the O(3) planes of the oxygen 6-rings; two at Tl(3) are in the sodalite unit, 1.69 Å from the [111] plane at O(3). Tl(1) and Tl(3) are trigonally coordinated to their respective sets of three O(3) framework oxygens at 2.62 and 2.70 Å. The principal cation positions, Tl(1) and Tl(3), agree well with those of the dehydrated structure in the previous investigation.[8]

The remaining ion at Tl(4) is located relatively deep within the large cavity, 2.66 Å from the [111] plane at O(3). Its closest approach to a framework atom, to an O(2) of a 6-ring otherwise empty on the large cavity side, is 3.21 Å; this is 0.42 Å greater than the sum of the corresponding ionic radii[7] and approximately 0.5 Å greater than the primary framework approach made by any of the other three kinds of Tl^+ ions. Tl(4) also approaches two O(3) ions of the same 6-ring at 3.23 Å (see Figure 2). The relatively large thermal parameter of the ion at Tl(4) is consistent with its long and apparently weak interaction with the zeolite framework. (A contribution to the large thermal parameters of both Tl(2) and Tl(4) is likely to result from the simplifying assumption of *Pm*3*m* symmetry made in structure analysis, although the thermal ellipsoids appear to be consistent with their environments without invoking this consideration.) Tl(4) is unable to make a more favorable approach to the 6-ring because of the presence of a Tl(3) ion on the opposite side of this ring in the sodalite unit.

To minimize Tl^+-Tl^+ repulsions, it is necessary that Tl(4) and the two ions at position Tl(3) be associated with the same threefold axis (that is, associated with two opposite 6-rings of the large (or small) cavity), while the six Tl(1)'s occupy the six remaining 6-oxygen rings per unit cell. The two Tl^+ ions at Tl(3) in the sodalite unit must be on opposite sides of the origin; also Tl(4) and an ion at Tl(3) must be on opposite sides of the same 6-ring so that the actual intercationic distances are as large as possible: Tl(3)-Tl(3) = 4.40 Å and Tl(4)-Tl(3) = 4.43 Å.

The dehydrated structures of Tl_{12}-A and Tl_{11}-A[13] differ by more than the placement of the twelfth ion at Tl(4). The occupancies of the Tl^+ ions associated with 6-rings at Tl(1) and Tl(3) have changed from seven and one, respectively, in dehydrated Tl_{11}-A,[8] to six and two in Tl_{12}-A.

The lack of agreement between the sum of the ionic radii of Tl^+ and O^{2-}, 2.79 Å, and those observed, 2.62, 2.71, and 2.70 Å, involving Tl(1), Tl(2), and Tl(3), respectively, is primarily a result of the unusually low ligancy of these cations in the dehydrated structure. Similar situations have been observed in other zeolite A structures.[1,2,8,13,22]

The unusually situated ion at Tl(4) results from the same structural considerations which caused some cations to be zero-coordinate in the dehydrated structures of K_{12}-A,[1] $Rb_{11}Na_1$-A,[2,3] and Cs_7K_5-A[4]—that is, all possible coordination sites are filled with large monovalent cations before all negative charges of the framework have been balanced (see ref 2). In each of these three structures, the twelfth (zero-coordinate) cation occupies a threefold axis position deep within the large cavity, 1.5 Å or more than the sum of the appropriate ionic radii[7] from its nearest neighbor. Thallous ions, however, because of their greater covalent character as compared to alkali metal ions, have adopted an arrangement in which the twelfth Tl^+ ion occupies a position off the threefold axis where it can approach, at a distance too long by only 0.4 to 0.5 Å, two O(3)'s and an O(2) of a 6-ring (see Figure 2). The ion at Tl(4) can, then, be considered intermediate between a very weakly held three-coordinate (but far from trigonal) cation, and a zero-coordinate one. Its chemical properties, with respect to further complexation for example, should therefore be extreme.

Another demonstration of the greater covalency of Tl^+, as compared to Rb^+ for example, is provided by a comparison of

8-ring cation sites in dehydrated $Rb_{11}Na_1$-A and Tl_{12}-A. Although the cationic radii are the same,[7] 1.47 Å, Tl(2) lies off (0,½,½) while Rb(2) does not, resulting in Rb-O 8-ring distances that are considerably longer than the corresponding shortest Tl-O distance. This demonstrates the greater tendency of Tl^+ to maintain some relatively short approach distances to framework oxide ions, and agrees with the observed reluctance of a twelfth Tl^+ ion to move to a position of unambiguous zero-coordination.

The crystal studied was dehydrated, Tl(4) cannot be attributed to residual water molecules. The dehydration conditions employed were more than sufficient to remove all water from Na^+, K^+, Rb^+, Co(II), and Mn(II) exchanged zeolite A.[23] If Tl(4) were occupied by water molecules instead of a Tl^+ ion, the hydration distance to Tl(1) would be 1.35 Å, far from the values near 2.86 Å found in hydrated Tl_{13}-A.

It appears that the assumption made in previous work,[8] that full Tl^+-exchange had been achieved, and that the composition of the zeolite A framework was therefore $Al_{11}Si_{13}O_{48}{}^{11-}$, was incorrect. The correct unit cell composition was probably $Tl_{11}NaAl_{12}Si_{12}O_{48}$.

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Supplementary Material Available: Listings of the observed and calculated structure factors for both structures (Supplementary Tables 1 and 2) (4 pages). Ordering information is given on any current masthead page.

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Flash Photolysis Studies of *N*-Chloro- and *N*-Nitrosopiperidine in Aqueous Solution. Assignment and Reactivity of the Piperidinium Radical[1a]

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Abstract: Flash photolyses of *N*-chloro- and *N*-nitrosopiperidine in acidified aqueous solution (pH ~2) gave a common transient with an average lifetime of $\tau = 124 \pm 10\ \mu s$, which was assigned as the piperidinium radical. The piperidinium radical exhibited monotonic increases of UV absorption from ~400 nm toward 280 nm and its lifetime was not affected by acidity changes in the 0.01-0.50 N range nor quenched by oxygen. The absolute reaction rate constants of hydrogen abstraction and addition of the piperidinium radical on various substrates were determined by monitoring the decay kinetics of the transient. Flash photolysis studies of *N*-chloropiperidine are complicated by instability of the starting material under the conditions and by various transients generated in the chain processes. The latter complication was eliminated by low concentrations of *N*-chloropiperidine and the presence of oxygen. The implication of these effects to photodecomposition of *N*-chloro amines was discussed.

The aminium radical[3] (R_2NH^+) is an important reactive intermediate in the cyclization of N-halogenated amines (the Hofmann-Löffler reaction),[4-6] in the addition of chloro amines to olefins,[7,8] and in the chlorination of hydrocarbons and other organic compounds by chloro amines.[9-11] The mechanism of nitrosoamine photoreaction, which has been interpreted in terms of the chemistry of the aminium radical in the presence of nitric oxide,[12] has received further support from flash photolysis results on *N*-nitrosopiperidine (in the presence of dilute acid) in which direct evidence was obtained for the primary generation[13] of $R_2\dot{N}H^+$.

The chloro amine reactions are generally carried out in strongly acidic solutions such as sulfuric acid or sulfuric acid-acetic acid mixtures, and proceed by free-radical chain processes in which the aminium radical is the principal chain propagating species.[10,14] The primary step in the photolytically