(38) A. D. Berry, E. R. Corey, A. P. Hagen, A. C. MacDiarmid, F. E. Saalfeld, and B. F. Wayland, *J. Am. Chem. Soc.*, **92**, 1940 (1970).
(39) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).
(40) L. J. Guggenberger, D. D. Titus, M. T. Flood, R. E. Marsh, A. A. Orio, and H. B. Gray, *J. Am. Chem. Soc.*, **94**, 1135 (1972).
(41) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 2276 (1974).
(42) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973).
(43) G. Herzberg, "Spectra of Diatomic Molecules", 2nd ed, Van Nostrand, New York, N.Y., 1950, p 522.
(44) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).
(45) S. Cradock, E. A. Ebsworth, and A. Robertson, *J. Chem. Soc., Dalton Trans.*, 22 (1973).
(46) M. F. Guest, B. R. Higginson, D. R. Lloyd, and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 2*, **70**, 902 (1975).
(47) A. G. Robiette, G. M. Sheldrick, R. N. F. Simpson, B. J. Aylett, and J. A. Campbell, *J. Organomet. Chem.*, **14**, 279 (1968).
(48) K. Emerson, P. R. Ireland, and W. T. Robinson, *Inorg. Chem.*, **9**, 436 (1970).
(49) W. T. Robinson and J. A. Ibers, *Inorg. Chem.*, **6**, 1208 (1967).

# Zero-Coordinate $K^+$. Crystal Structure of Dehydrated Cesium and Potassium Exchanged Zeolite A, $Cs_7K_5$-A

**Roger L. Firor and Karl Seff***

*Contribution from the Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822.* *Received October 19, 1976*

**Abstract:** The structure of vacuum-dehydrated $Cs_7K_5Al_{12}Si_{12}O_{48}$, zeolite A with all $Na^+$ ions replaced by $Cs^+$ and $K^+$ as indicated, has been determined by single-crystal x-ray diffraction techniques in the cubic space group $Pm3m$ ($a$ = 12.266 (2) Å). The final weighted $R$ index is 0.047. In the structure, three $Cs^+$ ions fill an equipoint at the very centers of the oxygen 8-rings. Three other equivalent $Cs^+$ ions and three equivalent $K^+$ ions occupy respective equipoints on threefold axes opposite 6-rings in the large cavity. The three remaining cations lie on one unique threefold axis. Two of these, the $Cs^+$ ion and one $K^+$ ion, are located in the sodalite unit on opposite sides of the origin. *The remaining $K^+$ ion on this threefold axis is 4.40 Å from its nearest neighbors, three 6-ring oxide ions. This $K^+$ ion lies deep within the large cavity and can be considered zero coordinate by a distance criterion; its shortest approach to another ion exceeds the sum of the appropriate ionic radii by more than 1.7 Å.* 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 cation per unit cell, in this case $K^+$, must occupy a site remote from the anionic zeolite framework.

Zero-coordinate, large monovalent cations were observed in the crystal structures of dehydrated $K_{12}$-A[1,2] and $Rb_{11}Na_1$-A.[2,3,4] In dehydrated $K_{12}$-A,[1] one $K^+$ ion per unit cell was located deep within the large cavity, 4.25 Å from its nearest neighbors, three framework oxide ions of a 6-ring.[5] In dehydrated $Rb_{11}Na_1$-A,[3,4] one $Rb^+$ ion per unit cell occupies a similar position 4.35 Å from the 6-ring oxide ions. The closest ionic contacts of these monovalent cations to framework oxide ions are too long by at least 1.5 Å.[6] The term "zero coordination"[3,4] is employed to describe this discrepancy.

In this work, the third zeolite A crystal structure to contain a zero-coordinate cation is reported. Initial hopes that a higher degree of $Cs^+$ exchange would be attained, and that the zero-coordinate cation would be $Cs^+$, have not been realized. Nevertheless, the result reconfirms the existence of uncoordinated cations, $K^+$ in this case, and demonstrates again the conditions[3,4] necessary for their occurrence.

## Experimental Section

Crystals of zeolite 4A were prepared by a modification of Charnell's method,[7] including a second crystallization using seed crystals from the first synthesis. A single crystal 0.085 mm on an edge was lodged in a fine glass capillary. The crystal was first exchanged with 0.2 N KOH (Mallinckrodt, Analytical Reagent: $Na^+$, 0.05%; $NH_4^+$, 0.02%; all other cations, less than 0.01%) by flow methods—a continuous stream of fresh solution flowed past the crystal at a velocity of approximately 1.0 cm/s for a period of 2 days at 25 (1) °C. Next, the crystal was similarly exchanged with 0.1 N CsOH (Ventron/Alfa, 99.9% purity) for 12 days. After the solution was drained, no noticeable droplet of solution remained close to the crystal, and a rinse step, which might have caused some $H^+$ exchange, was not performed. After dehydration at 350 °C and $2 \times 10^{-6}$ Torr for 48 h, the crystal was allowed to cool to room temperature, and was sealed in its capillary, while still under vacuum, by torch. The microscopic appearance of the crystal was not altered by these exchange and dehydration procedures.

The dehydrated zeolite, with a unit cell composition of $Cs_7K_5Si_{12}Al_{12}O_{48}$ as determined by refinement of the diffraction data, will subsequently be referred to as $Cs_7K_5$-A.

**X-Ray Data Collection.** The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[8,9] Preliminary crystallographic experiments and subsequent data collection were performed with an automated, four-circle Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and a pulse-height analyzer. Molybdenum radiation was used for all experiments ($K\alpha_1$, $\lambda$ = 0.70930 Å; $K\alpha_2$, $\lambda$ = 0.71359 Å). The cubic unit cell constant, as determined by a least-squares refinement of 15 intense reflections for which $2° < 2\theta < 24°$, is 12.266 (2) Å.

Reflections from two intensity-equivalent regions of reciprocal space ($hkl$, $h \le k \le l$, and $lhk$, $l \le h \le k$) were examined using the $\theta$–$2\theta$ scan technique. Each reflection was scanned at a constant rate of 1.0 deg $min^{-1}$ from 0.8° (in $2\theta$) below the calculated $K\alpha_1$ peak to 0.8° above the $K\alpha_2$ maximum. Background intensity was counted at each end of a scan range for a time equal to half the scan time. Other details of the data collection and reduction[10] are the same as previously described.[4] No absorption correction was applied to the data. Of the 881 pairs of reflections examined for $Cs_7K_5$-A, only the 314 whose net counts exceeded three times their corresponding esd's were used in structure solution and refinement.

**Structure Determination.** Full-matrix least-squares refinement of the structure was initiated using the atomic parameters for the framework atoms ((Si,Al), O(1), O(2), and O(3)) and for $Cs^+$ which had previously been found in the crystal structure of $Cs_7Na_5$-A.[11] Anisotropic refinement of all ions, except those at Cs(1) and Cs(3) which remained isotropic, converged quickly to an $R_1$ index, $(\Sigma|F_o - |F_c||)/\Sigma F_o$, of 0.154 and a corresponding weighted $R_2$ index, $(\Sigma w(F_o - |F_c|)^2/\Sigma w F_o^2)^{1/2}$, of 0.187. (Refer to Table I and Figure 2 to identify these positions.) Simultaneous occupancy and thermal

**Table I.** Positional, Thermal,[a] and Occupancy Parameters for $Cs_7K_5$-A

| | Wyckoff position | $x$ | $y$ | $z$ | $\beta_{11}$ or $B_{iso}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Occupancy factor |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (Si,Al) | 24(*k*) | 0 | 1834 (2) | 3721 (2) | 24 (2) | 22 (2) | 18 (2) | 0 | 0 | 4 (3) | 1[b] |
| O(1) | 12(*h*) | 0 | 2248 (8) | ½ | 59 (11) | 57 (9) | 27 (8) | 0 | 0 | 0 | 1 |
| O(2) | 12(*i*) | 0 | 2946 (6) | 2946 (6) | 54 (9) | 36 (6) | 36 (6) | 0 | 0 | 3 (14) | 1 |
| O(3) | 24(*m*) | 1123 (4) | 1123 (4) | 3407 (5) | 36 (4) | 36 (4) | 61 (7) | 30 (9) | −5 (7) | −5 (7) | 1 |
| Cs(1) | 8(*g*) | 2702 (3) | 2702 (3) | 2702 (3) | 66 (2) | 66 (2) | 66 (2) | 49 (4) | 49 (4) | 49 (4) | ⅜ |
| Cs(2) | 3(*c*) | 0 | ½ | ½ | 115 (4) | 79 (2) | 79 (2) | 0 | 0 | 0 | 1 |
| Cs(3) | 8(*g*) | 823 (8) | 823 (8) | 823 (8) | 172 (11) | 172 (11) | 172 (11) | −134 (17) | −134 (17) | −134 (17) | ⅛ |
| K(1) | 8(*g*) | 2083 (9) | 2083 (9) | 2083 (9) | 87 (7) | 87 (7) | 87 (7) | 89 (19) | 89 (19) | 89 (19) | ⅜ |
| K(2) | 8(*g*) | 1300 (21) | 1300 (21) | 1300 (21) | 3.6 (8)[c] | | | | | | ⅛ |
| K(3) | 8(*g*) | 3656 (81) | 3656 (81) | 3656 (81) | 653 (149)[d] | 653 (149) | 653 (149) | 142 (388) | 142 (388) | 142 (388) | ⅛ |

[a] Positional and anisotropic parameters are given ×$10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant figure given for the corresponding parameter. The anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Occupancy for (Si) = ½; occupancy for (Al) = ½. [c] Isotropic thermal parameter in units of Å$^2$. [d] The corresponding root mean square displacements are 0.8 Å along the threefold axis and 0.7 Å normal to it.

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

| | | | |
|---|---|---|---|
| (Si,Al)-O(1) | 1.649 (4) | O(1)-(Si,Al)-O(2) | 106.9 (5) |
| (Si,Al)-O(2) | 1.662 (3) | O(1)-(Si,Al)-O(3) | 112.3 (4) |
| (Si,Al)-O(3) | 1.675 (2) | O(2)-(Si,Al)-O(3) | 107.2 (2) |
| | | O(3)-(Si,Al)-O(3) | 110.6 (4) |
| Cs(1)-O(3) | 2.873 (7) | (Si,Al)-O(1)-(Si,Al) | 144.2 (6) |
| Cs(1)-O(2) | 3.342 (3) | (Si,Al)-O(2)-(Si,Al) | 159.6 (7) |
| K(1)-O(3) | 2.326 (7) | (Si,Al)-O(3)-(Si,Al) | 143.5 (4) |
| K(1)-O(2) | 2.962 (5) | | |
| Cs(3)-O(3) | 3.212 (13) | O(3)-Cs(1)-O(3) | 87.2 (2) |
| Cs(3)-O(2) | 3.820 (14) | O(3)-K(1)-O(3) | 116.8 (8) |
| K(2)-O(3) | 2.60 (2) | O(3)-Cs(3)-O(3) | 76.2 (2) |
| K(2)-O(2) | 3.27 (2) | O(3)-K(2)-O(3) | 99 (1) |
| Cs(2)-O(1) | 3.376 (9) | O(3)-K(3)-O(3) | 53 (2) |
| Cs(2)-O(2) | 3.562 (10) | | |
| K(3)-O(1) | 5.08 (9) | | |
| K(3)-O(2) | 4.64 (13) | | |
| K(3)-O(3) | 4.40 (15) | | |
| K(2)-Cs(3) | 4.51 (5) | | |
| K(3)-Cs(3) | 6.0 (2) | | |
| K(3)-Cs(2) | 5.05 (2) | | |
| K(3)-K(1) | 5.89 (2) | | |
| K(3)-Cs(1) | 6.42 (12) | | |

[a] Numbers in parentheses are the estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

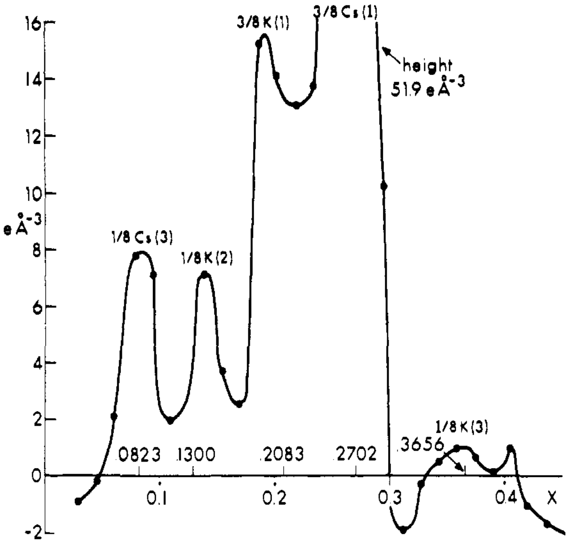

**Figure 1.** The electron density along the mean threefold axis of the unit cell, calculated using the observed structure factors. This function demonstrates the end result of the crystallographic work. It is subsequently factored onto eight threefold axes for which $0 < x < 0.5$ by the principle of the minimization of intercationic repulsions. The corresponding difference function, in which all of the ions shown are subtracted except for the ion at K(3), shows only two peaks, one at K(3) nearly as shown above, and the other of comparable size at the Cs(1) positions.

parameter refinement of these $Cs^+$ positions clearly indicated 2.8 ions at Cs(2), 3.3 at Cs(1), and 1.2 at Cs(3). This constitutes a crystallographic determination of the presence of seven $Cs^+$ ions per unit cell. By the assumption of stoichiometry, these values were rounded to the integers 3, 3, and 1, respectively, and were held fixed thereafter, except for one later check.

Subsequent least-squares refinement included two $K^+$ ion positions, K(1) and K(2), with occupancies of 3 and 1, respectively. These positions were based on similar positions from the structure of dehydrated $K_{12}$-A[1]. Framework and all cation positions were refined anisotropically (except for K(2), isotropically), to $R_1$ and $R_2$ indices of 0.082 and 0.059, respectively.

A difference Fourier synthesis based on this 11-cation model revealed a possible position for the 12th cation (either a $Cs^+$ or $K^+$) on the threefold axis at $x = 0.36$, and 1.2 e Å$^{-3}$ in height with an estimated standard deviation of 0.11 e Å$^{-3}$. Except for this peak, the map was remarkably featureless except for residual density very near the positions of K(1) and Cs(1). This position at $x = 0.36$, indicative of a zero-coordinate cation, was stable in anisotropic least-squares refinement as one $K^+$ ion, and lowered the error indices $R_1$ and $R_2$ to 0.072 and 0.047, respectively. (Refinement of this position as one $Cs^+$ ion was unstable in least squares.) The addition of this 12th cation lowered $R_1$ by 0.010 and $R_2$ by 0.012, significant amounts. At this point, simultaneous positional and temperature factor refinement of all cations, and occupancy refinement of all threefold cations, resulted in occupancies very near those shown in Table I with little change in error indices. These occupancy parameters placed 2.92 (8) ions at Cs(1), 3.0 ions at Cs(2) (held fixed), 1.03 (3) at Cs(3), 2.6 (2) at K(1), 0.6 (1) at K(2) with a near-zero thermal parameter (this indicates that the occupancy value of 0.6 is somewhat too small due to correlation in least squares), and 1.1 (4) ions at K(3). Finally, a last three cycles of least-squares refinement allowed the positional and temperature factors to vary while occupancies remained fixed at the values shown in Table I.

The goodness-of-fit, $(\Sigma w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 2.45; $m$ (314) is the number of observations, and $s$ (37) is the number of variables in least squares. All shifts in the final cycle of least-squares refinement were less than 0.2% of the corresponding esd's.

For $Cs_7K_5$-A, the largest peak on the final difference Fourier function, whose estimated standard deviation is 0.10 e Å$^{-3}$, was 1.6 e Å$^{-3}$ on the threefold axis at $x = 0.25$, very near Cs(1). This small residual peak is not unusual, and can be attributed to the particularly anharmonic thermal motion to be expected for ions whose nearest neighbors are all at one side. Moreover, and in addition to the crystallographic arguments, the placement of a $K^+$ ion at this position would require it to be no more than 3.56 Å from another cation, at Cs(3), an unreasonably short approach, especially since it would be

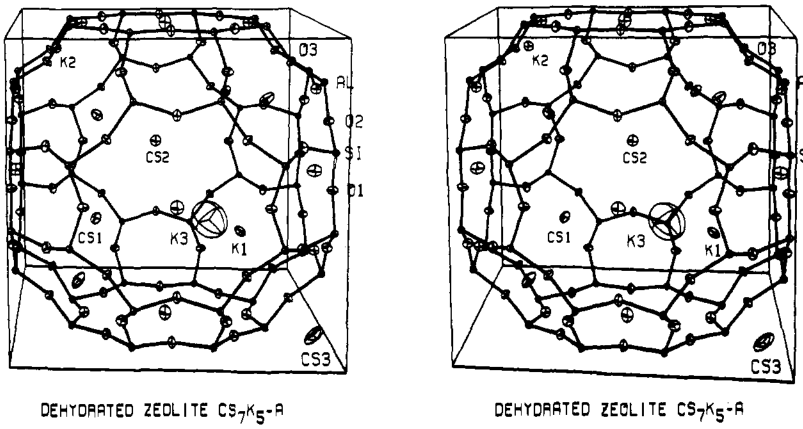

**Figure 2.** A stereoview of $Cs_7K_5$-A showing a likely atomic arrangement in a particular unit cell. It is consistent with the disordered structural model[17] which has emerged from the crystallographic calculations, is discussed in the text, and is depicted in this and subsequent figures. Ellipsoids of 20% probability are shown.

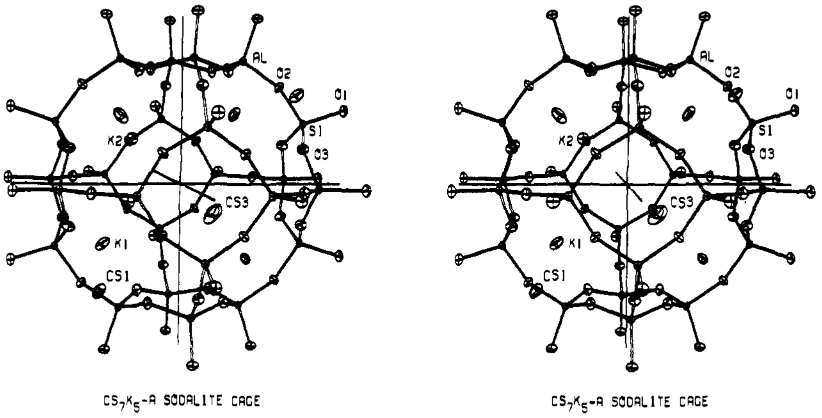

**Figure 3.** A stereoview of the sodalite cavity of $Cs_7K_5$-A. Ellipsoids of 20% probability are shown.

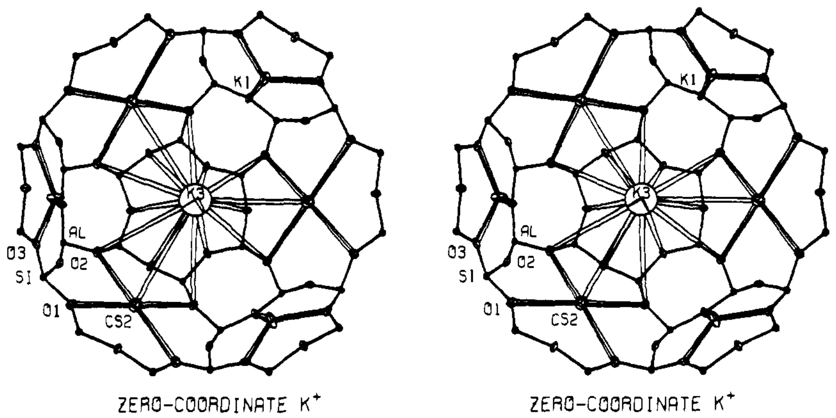

**Figure 4.** A stereoview, approximately along the threefold axis, of half of the large cage, showing all K(3)-O distances less than 5.1 Å and all K(3)-(Cs or K) distances less than 5.9 Å. The Cs(3) ion which is 6.0 Å from K(3) along the direction of view is eclipsed. Ellipsoids of 20% probability are shown.

an unmoderated cation-cation approach with the nearest anions far to the sides.

The final structural parameters are presented in Table I. Interatomic distances and angles are given in Table II. A listing of observed and calculated structure factors is available; see paragraph at end of paper regarding supplementary material. Figure 1 shows the mean of the electron density distributions along the threefold axes of the unit cell. The structure is shown in Figures 2, 3, and 4.

The full-matrix least-squares program used[10] minimized $\Sigma w(\Delta|F|)^2$; the weight ($w$) of an observation was the reciprocal square of $\sigma$, its standard deviation. Atomic scattering factors[12] for $Cs^+$, $K^+$, $O^-$, 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 real component ($\Delta f'$) of the anomalous dispersion correction.[13]

## Discussion

In the structure of $Cs_7K_5$-A, three $Cs^+$ ions at Cs(2) are located at the centers of the planar 8-oxygen rings at sites of $D_{4h}$ symmetry, 3.37 Å from four O(1) oxygens and 3.56 Å from four O(2)'s. The sum of the ionic radii[6] of $Cs^+$ and $O^{2-}$ is less, 3.01 Å.

A unique relative distribution of the remaining nine cations along the four threefold axes results when the cations are placed within their partially occupied equipoints so as to

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

| | |
|---|---|
| K(1) | 0.42 |
| K(3)[b] | 3.76 |
| K(2)[c] | −1.24 |
| Cs(1) | 1.74 |
| Cs(3)[b,c] | −2.25 |

[a] A negative deviation indicates that the atom lies on the same side of the plane as the origin. [b] These two ions are associated with the same 6-ring. [c] These two ions are associated with two 6-rings on opposite sides of the sodalite units.

minimize intercationic repulsions. This arrangement is depicted in the figures. The two cations at K(2) and Cs(3) lie in the sodalite unit on the same threefold axis, on opposite sides of the origin. They are opposite 6-rings, 1.24 and 2.26 Å, respectively, from the [111] planes at O(3). The three ions at K(1), which are in the large cavity 0.42 Å from the O(3) planes of 6-rings, occupy those three of the remaining six 6-rings which are closer to K(3), the zero-coordinate cation, because the K(3)–K(1) distance is 1.10 Å longer than K(3)–Cs(1) would be. The three Cs(1) ions occupy large cavity sites, 1.74 Å from the O(3) planes of the remaining three 6-rings, sharing threefold axes with the three K(1) ions and on the opposite side of the large cavity from them. The two cations at Cs(3) and K(3) must be on opposite sides of the same 6-ring. This model allows the shorter intercationic distances to be as large as possible: Cs(3)–K(3) = 6.0 Å, Cs(3)–K(2) = 4.51 Å, and K(3)–K(1) = 5.89 Å.

The zero-coordinate cation, K(3), lies deep within the large cavity, 3.76 Å from the O(3) plane. Its closest approach to framework atoms (to three O(3)'s of a 6-ring) is 4.40 Å, which is 1.75 Å greater than the sum of the corresponding ionic radii.[6] The large thermal parameter for this $K^+$ ion is similar to, but somewhat smaller than, those of K(3) and Rb(3), the zero-coordinate ions in dehydrated $K_{12}$-A[1] and $Rb_{11}Na_1$-A,[3,4] respectively. Perhaps it is smaller because the $Cs^+$ ions at Cs(2) are at the very centers of the 8-rings, and are therefore closer to the uncoordinated $K^+$ ion than are the corresponding 8-ring $K^+$ ions in dehydrated $K_{12}$-A; these latter three $K^+$ ions lie off the centers of the 8-rings and are farther from the uncoordinated $K^+$ ion at K(3). (See the approach made by three Cs(2)'s to K(3) in Figure 4.)

The electron density at K(3) cannot be attributed to residual water molecules; the crystal studied was dehydrated. The dehydration conditions employed were more than sufficient to remove all water from $Na^+$-,[14] $K^+$-,[1] $Rb^+$-,[3,4] Co(II)-,[5a,14,15] and Mn(II)-exchanged[15] zeolite A.[16] Upon dehydration, 12 cations must remain in the unit cell, and occupancy refinement definitively supports that number. Quite apart from the crystallographic result, a consideration of the structure indicates that a position obviously more plausible than the one at K(3) does not exist for the 12th cation per unit cell—that position is needed to account for all of the cations.

As noted in the preliminary report of the structure of dehydrated $Rb_{11}Na_1$-A,[3] the stability of an ion at K(3) cannot be explained using only electrostatic considerations. The application of the Laplace equation, $\nabla^2 V = 0$, to this system indicates that a purely electrostatic potential energy minimum for a cation can exist only *at* the position of an anion, and cannot exist at any other position, such as K(3). Apparently, the usual chemical attractive and repulsive forces have balanced to give a shallow energy minimum at the position K(3).

Figure 4 shows the ion at K(3) in relation to its nearest neighbors, which are either members of the nearest 6-ring or are arranged symmetrically about it. K(1) is 4.40 Å from three ions at O(3), 4.64 Å from three at O(2), 5.05 Å from three at Cs(2), 5.08 Å from six at O(1), 5.89 Å from three at K(1), 6.0 Å from a single ion at Cs(3), and 6.42 Å from three at Cs(1).

As in dehydrated $K_{12}$-A[1] and $Rb_{11}Na_1$-A,[3,4] it is necessary that the ions at K(3), K(2), and Cs(3) be placed on the same threefold axis to minimize intercationic repulsions. These three ions, then, share two 6-rings per unit cell on opposite sides of the small (or large) cavity. The three K(1)'s are located in the three (of the remaining six per unit cell) 6-rings nearest K(3), while the three Cs(1) ions occupy the three remaining 6-rings.

The ions at Cs(1), K(1), Cs(3), and K(2) are trigonally coordinated to their respective sets of three O(3) oxygens at 2.87, 2.33, 3.21, and 2.60 Å. Because of the disorder implicit in the structure,[16] only an average O(3) position was determined and could be used to calculate these distances, although one would expect the conformation of a particular 6-oxygen ring to depend upon the identity and position of the cation(s) associated with it. In $Cs_7K_5$-A, four chemically nonequivalent 6-rings exist, but only the average conformation over eight such rings can be determined. Accordingly, distances and angles involving O(3), e.g., the short K(1)–O(3) distance, may be somewhat in error. However, the Cs(1)–O(3) distance is also short, shorter by approximately 0.1 Å than the Cs–O(3) distance in $Cs_7Na_5$-A.[11] These unusually short approaches may result from the inability of the large 6-ring cations, $K^+$ and $Cs^+$, to lie near the planes of their three nearest oxide neighbors, or more generally, from the diminished ability of these 12 large cations to approach the anionic charge they balance, as compared to that of the $Na^+$ ions in dehydrated $Na_{12}$-A,[5a] for example. The unusually low ligancies of the cations in this dehydrated structure also contribute to such short distances. Bonds shorter than the sum of the appropriate ionic radii are common in dehydrated zeolite A structures which contain large monovalent cations. Examples include $K_{12}$-A,[1] $Rb_{11}Na_1$-A,[3,4] $Cs_7Na_5$-A,[11] and $Tl_{12}$-A.[17]

It is not clear why it is a $K^+$ ion and not a $Cs^+$ ion that occupies a zero-coordinate position. If a $Cs^+$ ion occupied the zero-coordinate position, the sodalite unit could contain two $K^+$ ions which could be farther apart than one $Cs^+$ and one $K^+$ ion. Also, a $K^+$ ion is able to approach the anionic zeolite framework more closely. Perhaps this structure has occurred because a Cs–O bond is stronger[18] than a K–O bond by approximately 10 kcal/mol.

Although the flow conditions employed for the exchange of $Cs^+$ from aqueous solution into $K_{12}$-A are considered much more strenuous than the static procedure[11] used to exchange $Cs^+$ into $Na_{12}$-A, the same ion-exchange limit was encountered. Apparently, the eighth $Cs^+$ ion to enter the unit cell would occupy a markedly less favorable position; the seventh might complete the occupation of a comparatively stable equipoint. Considering the large size of the $Cs^+$ ion, an exchange limit based on three $Cs^+$ ions filling the 8-ring sites and four $Cs^+$ ions associated with tetrahedrally arranged 6-ring sites, half filling them, as was proposed for hydrated $Cs_7Na_5$-A,[11] appears to apply to hydrated $Cs_7K_5$-A as well. By a similar symmetry argument, a limiting number of seven xenon atoms is found[19] associated with the 6- and 8-rings of $Ca_4Na_4$-A at −133 °C.

Of the three dehydrated zeolite A structures so far determined which show zero coordination, $Cs_7K_5$-A represents the least favorable experimental situation. It shows one zero-coordinate $K^+$ ion (18 $e^-$) resolved from threefold axis electron density representing four $Cs^+$ and five $K^+$ ions (306 $e^-$); the ratio is 0.059. In $K_{12}$-A, one $K^+$ ion was located amidst a threefold axis arrangement of nine $K^+$ ions (162 $e^-$); the ratio is 0.111. In $Rb_{11}Na$-A, the corresponding numbers are 36 and 298 $e^-$, with a ratio of 0.121. The considerations of (1) the particularly large thermal parameters of the zero-coordinate cations, (2) the relatively manageable but pervasive disorder in the zeolite framework due to the assumption of the equivalence of Si and Al ions and their environments,[16] and (3) the relatively small fraction of threefold axis scattering matter due to the zero-coordinate cation, make this determination the least definitive of the three, and worthy of further concern. However, the detailed agreement of the positional and thermal parameters of the zero-coordinate cation found here with those found in the previous two structures, coupled with newer results in dehydrated $Tl_{12}$-A,[17] affirms the present result and allows it to constitute a reconfirmation of the existence of zero coordination.

## Conclusion

Zero-coordinate cations, as have been found in dehydrated $K_{12}$-A,[1] dehydrated $Rb_{11}Na_1$-A,[3,4] and now in dehydrated $Cs_7K_5$-A, occur when well-defined conditions involving the zeolite and the cations are satisfied. Briefly, zero coordination occurs when all of the coordination sites available to large cations in the zeolite framework are filled before all anionic charges of the framework are balanced. By difference, one cation per unit cell remains uncoordinated. This has been discussed earlier[3,4] in greater detail.

As a working definition, similar to the distance criterion used to decide whether a significant hydrogen bonding interaction exists, an ion is considered not coordinated to another ion if the distance between them exceeds the sum of their corresponding radii by more than 1.0 Å.[3] At least, the bond order is much less than one. On this basis, the ion at K(3) is termed zero coordinate, zero being the sum of integers, all zero, describing its bond orders to its nearest neighbors.[3] For this particular structure, the distance discrepancy, 1.75 Å, is substantially larger that the value of 1.0 Å used in the criterion.

It appears that zero-coordinate cations can be found in any dehydrated sample of $K_rRb_sCs_t$-A, where $r + s + t = 12$ for charge balance. As in $Rb_{11}Na$-A, zero coordination may persist when one or more smaller exchangeable cations are present per unit cell.

**Acknowledgments.** This work was supported by the National Science Foundation (Grant MPS73-08761). We are indebted to the University of Hawaii Computing Center.

**Supplementary Material Available:** Listings of the observed and calculated structure factors (supplementary table) (2 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) P. C. W. Leung, K. B. Kunz, I. E. Maxwell, and K. Seff, *J. Phys. Chem.*, **79**, 2157 (1975).
(2) The nomenclature refers to the contents of the unit cell. For example, $Cs_7Na_5$-A represents $Cs_7Na_5Al_{12}Si_{12}O_{48}$, exclusive of water molecules if a hydrated crystal is considered.
(3) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **98**, 5031 (1976).
(4) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 1112 (1977).
(5) A discussion of zeolite nomenclature is available: (a) R. Y. Yanagida, A. A. Amaro, and K. Seff, *J. Phys. Chem.*, 77, 805 (1973); (b) L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, **82**, 1041 (1960).
(6) "Handbook of Chemistry and Physics", 55th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1974, p F190.
(7) J. F. Charnell, *J. Cryst. Growth*, **8**, 291 (1971).
(8) K. Seff, *J. Phys. Chem.*, **76**, 2601 (1972).
(9) P. E. Riley, K. Seff, and D. P. Shoemaker, *J. Phys. Chem.*, **76**, 2593 (1972).
(10) Principal computer programs used in this study: T. Ottersen, COMPARE data reduction program, University of Hawaii, 1973; full-matrix least squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLA LS4, American Crystallographic Association Program Library (old) No. 317 (revised 1976); Fourier program, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971; C. K. Johnson, ORTEP, Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(11) T. B. Vance, Jr., and K. Seff, *J. Phys. Chem.*, **79**, 2163 (1975).
(12) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, pp 73–86.
(13) Reference 12, pp 149–150.
(14) R. Y. Yanagida, T. B. Vance, Jr., and K. Seff, *Inorg. Chem.*, **13**, 723 (1974).
(15) P. E. Riley and K. Seff, *Inorg. Chem.*, **13**, 1355 (1974).
(16) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).
(17) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 4039 (1977).
(18) I. Brewer and E. Brackett, *Chem. Rev.*, **61**, 425 (1961).
(19) K. Seff, Ph.D. Thesis, Massachusetts Institute of Technology, 1964.

---

# Asymmetric Synthesis. Interligand Chiral Recognition between Prochiral Olefins and a Chiral Sulfoxide Coordinated to Platinum(II)

**Heather Boucher and B. Bosnich***

*Contribution from the Lash Miller Chemical Laboratories, Chemistry Department,
University of Toronto, Toronto, Ontario, M5S 1A1, Canada.*

*Received February 1, 1977*

**Abstract:** A series of complexes of the type *cis*-[Pt((*S*)-TMSO)(olefin)$Cl_2$] where, TMSO is *p*-tolyl methyl sulfoxide, have been prepared and characterized. The object was to determine to what extent chiral sulfoxide ligands were capable of distinguishing the prochiral faces of coordinated olefins, and whether chiral sulfoxides might prove useful for metal assisted asymmetric synthesis. By a variety of techniques, the absolute configurations of the (coordinated) olefins were assigned, and the extent of chiral induction was determined quantitatively. The amount of chiral induction was found to be generally small. However, quite large discrimination was observed for the olefinic rotation barriers of the *R* and *S* olefin diastereomers; in all cases studied, the *S* olefin appeared to rotate much more quickly than the *R* olefin diastereomer. The reasons for this and other chiral effects are suggested and their significance to the design of metal complexes for asymmetric synthesis is discussed.

Transition metal complexes, because of their simplicity and ready susceptibility to subtle variation, provide attractive reagents for asymmetric syntheses of organic molecules.[1-3] Of particular note are the modified versions of Wilkinson's catalyst, for which very high optical yields for the catalytic hydrogenation of prochiral olefins have been reported.[4,5] Although symmetry dictates that any chiral reagent will distinguish between the enantiotopic groups or faces of a prochiral substrate,[6] the rational design of asymmetric systems which give high optical yields requires a fairly detailed understanding