peaks were too low to permit high resolution data to be obtained, they have the nominal masses of $N_3H_5^+$ and $N_3H_4^+$. These results are entirely consistent with the structure of the zeolite complex—compared to triazane, cyclotriazane complexes Ag^+ at a longer distance and has easier access to the principal zeolite channels. Cyclotriazane would therefore be less tightly held within the zeolite and should be easier to remove than triazane.

The net reaction has not yet been determined. Hydrogen gas, an expected product, is not observed in sufficient quantity even upon heating. It appears that two Ag^+ ions have been reduced by one lattice O^{2-} to form the elements which migrated out of the zeolite during the dehydration step, and that two more Ag^+ ions have been reduced by NH_3 to form two more Ag atoms and two NH_4^+ ions during the sorption and reaction steps. Two NH_4^+ cations have been located at N(5) in the small cubic cavity, a novel site, where they form suitable hydrogen bonds to the zeolite framework: N(5)-O(1) = 2.59 (5) N(5)-O(3) = 2.7 (7) Å (see Table I, footnote *g*). Experiments designed to isolate N_3H_3 and N_3H_5 in pure form are in progress.

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Supplementary Material Available: A listing of observed and calculated structure factors (1 page). Ordering information is given on any current masthead page.

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Near-Zero-Coordinate, Three-Coordinate, and Four-Coordinate Europium(II). Bonding Effects Involving Europium(II) Valence Orbitals. Crystal Structure of Dehydrated Near-Fully Europium(II)-Exchanged Zeolite A

Sir:

The structures of a number of zeolite A crystals which have been incompletely exchanged with divalent cations show that these cations are all located at 6-ring[1] sites. This is true for Ca_4Na_4–A[2,3] and other structures containing Mn(II),[4,5] Co(II),[5,6] and Zn(II).[5,7] It was anticipated that divalent cations is more completely exchanged zeolite A structures, $M_x^{2+}Na_{12-2x}$–A, $5 \leq x \leq 6$, would also all locate at 6-ring sites. This expectation is now shown to be incorrect. In dehydrated Eu_xNa_{12-2x}–A, where x is ~5.75, one Eu(II) ion per unit cell is located in the plane of an 8-ring, surprisingly at a site of near-zero coordination.

Zero coordinate and near-zero coordinate monovalent cations have been well documented crystallographically in zeolite A,[8-12] and the principles governing their existence have been discussed.[9,10,12] Somewhat different principles describe the near-zero coordination of divalent ions. To learn more about these principles, and to further support this work with Eu(II), the crystal structures of dehydrated Ca_6–A and Sr_6–A have subsequently been determined.[13] In both, one near-zero-coordinate cation per unit cell is found at an 8-ring site. In Ca_6–A and Sr_6–A, the near-zero-coordinate Ca^{2+} and Sr^{2+} ions are 0.77 and 0.52 Å farther, respectively, from the nearest framework oxide ions (two O(1)s and one O(2); see Figure 1) than the sum of the appropriate ionic radii[14] would indicate. The corresponding discrepancy reported here for Eu(II) is 0.96 Å. This last result is particularly reliable because of the large scattering factor of Eu(II) for x rays.

A single crystal of sodium zeolite 4A, Na_{12}–A, 0.09 mm on an edge, was lodged in a fine glass capillary. $Eu(OH)_2$ was synthesized by the method of Bärnighausen[15] under anoxic conditions. Ion exchange was performed in the dark under nitrogen by allowing a saturated aqueous solution of $Eu(OH)_2$ to flow past the crystal at nearly 1.0 mm/s for 3 days. The crystal, whose appearance was not altered by this exchange procedure, was then dehydrated for 48 h at 350 °C and 5×10^{-6} Torr. Microscopic examination indicated that the crystal was still clear and undamaged, but that it had developed a bright orange color. It is considered unlikely that any Eu(II) was oxidized in any way, including by reaction with water, to form Eu(III); in fact, the reverse has been demonstrated intrazeolitically.[16]

The space group $Pm3m$ (no systematic absences) was used throughout this work for reasons discussed previously.[1a] The structure, a = 12.296 (2) Å at 23 (1) °C, was solved using 370 unique observed ($I_o > 3\sigma(I_o)$; $3° < 2\theta < 70°$) reflections collected by counter methods using a fully automated Syntex $P\bar{1}$ diffractometer with monochromatic Mo Kα radiation (Kα_1, $\lambda = 0.70930$ Å; Kα_2, $\lambda = 0.71359$ Å) and a pulse-height analyzer. Other experimental details including data reduction are the same as previously presented.[7] The unit cell composition as determined by refinement of the diffraction data is $Eu_xNa_{12-2x}Si_{12}Al_{12}O_{48}$, where x is 5.75 ± 0.25; 6.0 is the maximum value, corresponding to complete exchange. This dehydrated material will subsequently be referred to as Eu–A.

Least-squares refinement[17] of Eu–A began using the atomic parameters of the atoms of the aluminosilicate framework: (Si, Al), O(1), O(2), and O(3).[18] In addition, a probable Eu(II) position at Eu(1) (see Table I), in the large cavity near the planes of the 6 rings, was included. A subsequent Fourier difference function revealed the presence of a Eu(II) ion at Eu(2) in the sodalite unit, and a peak ~5.7 e Å^{-3} in height at $(0,\frac{1}{2},\frac{1}{2})$. This peak, at the center of the 8 ring, was stable in least-squares refinement as one Eu(II) ion at Eu(3). An ion at Eu(4) was located on a subsequent electron density difference function. Simultaneous positional, occupancy, and anisotropic thermal parameter refinement of all Eu(II) ions resulted in an R_2 index of 0.112 and occupancies very near those shown in Table I. These occupancy parameters placed 3.19 (9) ions at Eu(1), 0.79 (6) ions at Eu(2), 0.96 (5) ions at Eu(3), and 0.74 (10) ions at Eu(4). By the assumption of stoichiometry, the first three values were rounded to the integers 3, 1, and 1, respectively. The occupancy of Eu(4) was fixed at 0.75 ions per unit cell because the error indices rose somewhat when one full ion was placed there, even though the thermal parameters were allowed to adjust. Anisotropic refinement of all atoms at the occupancies shown in Table I quickly converged to an R_2 weighted index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2}$, of 0.114 ($R_1 = 0.135 = \Sigma|F_o - |F_c||/\Sigma F_o$). A trial removal of Eu(3), the near-zero-coordinate cation, from least-squares

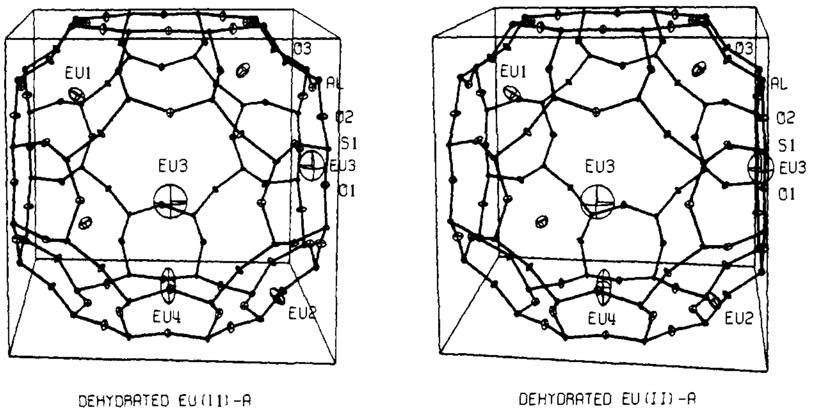

Figure 1. A stereoview of the Eu-A unit cell is shown. Selected bond lengths are (Si, Al)-O(1) = 1.645 (6), (Si, Al)-O(2) = 1.668 (5), (Si, Al)-O(3) = 1.669 (4), Eu(1)-O(3) = 2.358 (10), Eu(2)-O(3) = 2.427 (13), Eu(3)-O(1) = 3.376 (16), Eu(3)-O(2) = 3.653 (16), Eu(4)-O(1) = 2.25 (5), Eu(4)-O(3) = 2.24 (5) Å. Some bond angles are O(3)-Eu(1)-O(3) = 117.2 (6), O(3)-Eu(2)-O(3) = 112.0 (7), O(3)-Eu(4)-O(3) = 120 (1), O(1)-Eu(4)-O(1) = 121 (1), and O(1)-Eu(4)-O(3) = 76 (2)°. Ellipsoids of 20% probability are shown.

Table I. Positional, Thermal,[a] and Occupancy Parameters for Eu-A

Atom	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor
(Si, Al)	24 (k)	0	1828 (4)	3732 (3)	18 (3)	23 (3)	7 (3)	0	0	10 (5)	1[c]
O(1)	12 (h)	0	2254 (13)	½	32 (13)	36 (13)	21 (12)	0	0	0	1
O(2)	12 (i)	0	2899 (9)	2899 (9)	63 (16)	23 (8)	23 (8)	0	0	68 (21)[d]	1
O(3)	24 (m)	1113 (6)	1113 (6)	3427 (8)	33 (6)	33 (6)	25 (8)	64 (15)[d]	−22 (11)	−22 (11)	1
Eu(1)	8 (g)	2072 (5)	2072 (5)	2072 (5)	126 (5)	126 (5)	126 (5)	105 (12)	105 (12)	105 (12)	⅜
Eu(2)	8 (g)	1554 (14)	1554 (14)	1554 (14)	93 (11)	93 (11)	93 (11)	89 (27)	89 (27)	89 (27)	⅛
Eu(3)	3 (c)	0	½	½	351 (62)	508 (45)	508 (45)	0	0	0	⅓
Eu(4)	12 (j)	1757 (58)	1757 (58)	½	534 (105)	534 (105)	109 (52)	311 (280)	0	0	1/16[e]

[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 Figure 1 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] Root mean square displacements can be calculated from β_{ii} values using the formula, $\mu_i = 0.225\, a\, (\beta_{ii})^{1/2}$. [c] Occupancy for (Si) = ½; occupancy for (Al) = ½. [d] These values were decreased by 1σ in the preparation of Figure 1. [e] This number corresponds to 0.75 ions per unit cell.

refinement increased R_2 markedly, to 0.207. The final difference Fourier function was particularly featureless in the vicinity of the Eu(3) position. Atomic scattering factors[19] for Eu^{2+}, O$^-$ and (Si, Al)$^{1.75+}$ were used. The function describing (Si, Al)$^{1.75+}$ s the mean of the Si^0, Si^{4+}, Al^0, and Al^{3+} functions. An absorption correction was judged to be unnecessary and was not applied.

A likely arrangement of the Eu(II) ions in a particular unit cell is shown in Figure 1. This arrangement has not been established crystallographically and may not exist in every unit cell. It is consistent with the disordered structural model which emerged from the crystallographic calculations.

Four Eu(II) ions per unit cell are trigonally coordinated to 6 rings. Three of these, at Eu(1), are equivalent and lie in the large cavity, 0.40 Å from the O(3) planes, coordinated to their respective sets of three O(3)s at 2.36 (1) Å. The remaining three-coordinate ion at Eu(2) is located in the sodalite unit, 0.70 Å from the O(3) plane, with similar bond distances, 2.43 (1) Å to three O(3)s. These bond lengths agree well with the sum of the ionic radii for Eu(II) and O^{2-}, 2.41 Å.[14]

The ion at Eu(4) lies opposite a 4 ring. It is unusually four coordinate with its ligands all to one side, approaching two O(3)s and two O(1)s at approximately equal but somewhat short distances: Eu(4)-O(1) = 2.25 (5) and Eu(4)-O(3) = 2.24 (5) Å.

Finally, the near-zero-coordinate ion, Eu(3), is located at the very center of an 8 ring, 3.38 (2) Å from the nearest framework oxide ions (four O(1)s of an 8 ring). This approach is 0.96 Å greater than the sum of the corresponding ionic radii.[14] The ionic radius used for Eu(II), 1.09 Å,[14] agrees well with that obtained by extrapolation of Shannon's coordination-number-dependent ionic radii to a coordination number of four.[20] This 8-ring Eu(II) ion, because it is at the special position (0,½,½), has a tetragonal environment of symmetry D_{4h}, and is considered near-zero coordinate based on a distance criterion.[9]

The crystal structure of Eu-A has yielded the unexpected result that one Eu(II) ion per unit cell is located at a seemingly unfavorable 8-ring site, even though four generally preferred 6-ring sites remain unoccupied. Similar situations have subsequently been found in the crystal structures of Ca$_6$-A and Sr$_6$-A.[13] Apparently, some divalent ions locate at 8-ring sites for reasons which are largely electrostatic—to neutralize more evenly the anionic charge of the zeolite framework and to minimize intercationic repulsions. A dispersive (covalent) component to the bonding must be present also.[9,10]

In the crystal structures of Ca$_6$-A and Sr$_6$-A,[13] the near-zero coordinate 8-ring cations are located at (0,0.46,0.46) and (0.07,0.45,0.45), respectively, positions distinctly different from that of Eu(3) at (0,½,½). This difference is difficult to justify because of the almost identical ionic radii of Eu(II) and Sr^{2+}. McCarthy[21] demonstrated this near equality, which is almost independent of coordination number,[20] from a comparison of the unit cell volumes of a number of isostructural Sr^{2+} and Eu(II) ternary oxides. Therefore, the difference in 8-ring sites selected in Sr$_6$-A and Eu-A cannot be explained by the size of the ions—only if Eu(II) were significantly larger than Sr^{2+} could such arguments be used. Actually, Eu(II) is 0.02 Å smaller.[21]

It is concluded that the different electronic structures of Sr^{2+} and Eu(II) must be responsible for the different 8-ring sites selected by these ions. The Sr^{2+} ion has the krypton rare gas configuration, and Eu(II) has the Xe, $4f^7$ structure. Accordingly, the Eu(3) position must be stabilized by the interaction of a vacant Eu(II) valence orbital of the proper symmetry with the four nearest 8-ring oxide ions, at O(1), of the zeolite framework. The orbital should be 6s, 5d, or 4f in character, or a hybrid. Perhaps the Eu(II) $5d_{x^2-y^2}$ orbital, which is empty in the ground state, is most likely. The energy of this interaction does not need to be large to explain the positional differences observed.

The bright orange color of the crystal probably results from a Eu(II) f → d transition. For example, the $4f^7 \rightarrow 4f^6\ 5d$ electronic transition occurs in the near ultraviolet around 25 000 to 30 000 cm^{-1}.[22] Divalent rare earth ions doped into CaF_2 are known to be deeply colored because of the 4f → 5d transition.[22]

It may be expected that the near-zero-coordinate Eu(II) ion may be catalytically important because of its severe coordinative unsaturation. Indeed, this could be said of every Eu(II) ion in this structure. The 8-ring near-zero-coordinate Ca^{2+} ion in dehydrated Ca_6–A has been shown to be highly active in the isomerization of 1-butene.[23]

The relatively high final error indices for Eu–A can be attributed in part to the disorder present in the structure. Only the average ring geometries can be calculated, but there are three differently occupied kinds of 6 rings and two each differently occupied kinds of 8 and 4 rings. One would expect the conformation of a particular ring to depend upon whether or not it contains a Eu(II) ion. Empirically it is observed that the final error indices increase regularly for the series, Ca_6–A, Sr_6–A, and Eu–A. Ba_6–A decomposes upon dehydration. Together, these observations suggest increasing strain, disorder, and instability with increasing divalent cation size or mass.

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Supplementary Material Available: Listing of the observed and calculated structure factors (2 pages). Ordering information is available on any current masthead page.

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Correlation of Electrochemical Reactivity and Photoelectron Spectra of Aromatic Ketones

Sir:

Gooden and Brauman recently reported[1] on the photodissociation of butyrophenone radical cation and pointed out the possible connection between the photoelectron (pe) spectrum of the ketone and the kinetic sensitivity of the radical cation to incident radiation. These results prompt us to report a

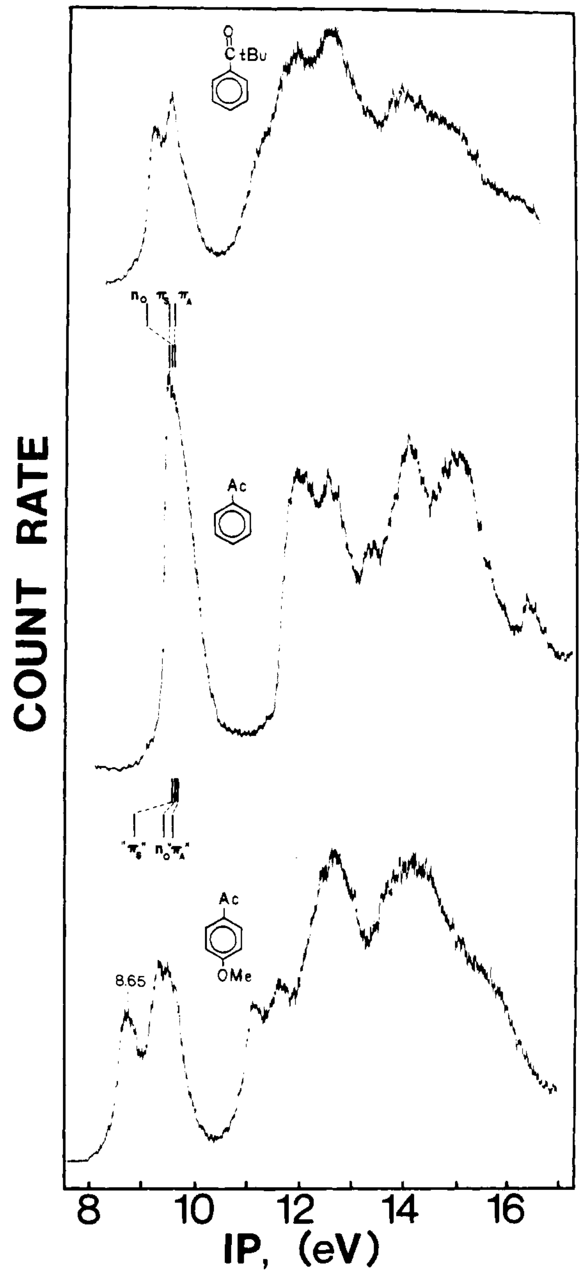

Figure 1. H(I) photoelectron spectra of phenyl *tert*-butyl ketone (top), acetophenone (middle), and *p*-methoxyacetophenone (bottom).