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Seven-Coordinate Distorted C_{3v}-Capped Trigonal-Prismatic Europium(II). Crystal Structure of Hydrated Europium(II)-Exchanged Sodium Zeolite A, Eu_5Na_2-A

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The crystal structure of hydrated Eu(II)-exchanged sodium zeolite A, Eu_5Na_2-A, has been determined by single-crystal X-ray diffraction techniques in the cubic space group *Pm*3*m*; $a = 12.290$ (2) Å. The structure was refined to the final error indices $R_1 = 0.120$ and R_2 (weighted) = 0.106. In the large cavity, 3.5 seven-coordinate Eu(II) ions per unit cell are found, 0.78 Å from O(3) planes, at a threefold-axis equipoint. Each coordinates to three O(3) oxide ions at 2.50 (1) Å and to three equivalent water molecules, which occupy a general equipoint deep within the large cavity, at 2.84 (5) Å. The seventh ligand of each of these Eu(II) ions, a water molecule which lies within the sodalite unit, completes a distorted C_{3v}-capped trigonal-prismatic coordination polyhedron. Altogether, that water equipoint contains 7.5 equivalent molecules per unit cell, 3.5 of which bond to the 3.5 Eu(II) ions through the 6-rings at 2.67 (4) Å. Also in the sodalite unit, along a threefold axis and 0.75 Å from an O(3) plane, lies a six- or seven- coordinate Eu(II) ion with an occupancy of 0.5 ion per unit cell. It is bound, at 2.50 (1) Å, to three framework oxide ions of a 6-ring and less strongly, at 2.95 (5) Å, to three of the water molecules in the sodalite unit; an additional unlocated water molecule in the large cavity may coordinate, as with the first kind of Eu(II) ion. Finally, the remaining Eu(II) ion is located on a mirror plane in the large cavity near the plane of an 8-ring. It forms three coordination bonds to two kinds of 8-ring oxides at 2.76 (3) and 2.70 (5) Å, respectively. Water molecules associated with this Eu(II) ion could not be located. Three disordered water molecules are found deep in the large cavity; they are apparently involved in hydrogen bonding to other unlocated water molecules. It appears that C_{3v}-capped trigonal-prismatic coordination had not been observed before for any cation.

Introduction

The structures of many trivalent lanthanide compounds with a wide range of coordination numbers and geometries are known.[1] However, the structural chemistry of the divalent lanthanides, including Eu(II) which is the most stable and the most studied, remains relatively undeveloped, presumably because its compounds are unstable with respect to oxidation to Eu(III) by trace amounts of O_2.

Europium(II) can be readily ion exchanged into crystals of zeolite A under anoxic conditions.[2] Subsequent reactions may then be performed and the response of Eu(II) can be observed crystallographically. Because the aluminosilicate framework of a zeolite behaves as a nearly inflexible polydentate ligand, unusual and unsatisfactory coordination geometries are commonly found for intrazeolitic cations.[3] Accordingly, zeolites are a unique medium in which to study the chemistry of Eu(II).

Previous crystal structure determinations of fully and incompletely dehydrated Eu(II)-exchanged zeolite A have shown Eu(II) ions in the following coordination situations: (1) three-coordinate nearly trigonal planar,[2,4] (2) four-coordinate nearly tetrahedral,[4] and (3) four-coordinate with all ligands at one side[2] (opposite a 4-oxygen ring).[5] Eu(II) is very coordinatively unsaturated in these structures.

The study of hydrated Eu(II)-exchanged zeolite A was undertaken primarily to determine the intrazeolitic coordination environment of Eu(II) in a more hospitable situation, one in which coordinative unsaturation is not likely. Several hydrated transition-metal-ion-exchanged zeolite A structures have been characterized, all of which have ions with unusual coordination numbers or geometries as a result of the zeolitic environment.[6-8] Accordingly, it was anticipated that the crystal structure of hydrated Eu(II)-exchanged zeolite A would contain Eu(II) ions in a novel coordination situation.

The results to be presented are based upon the largest data set (at the 3σ level) ever observed for a zeolite A structure.

Expermental Section

Single crystals of zeolite 4A, Na_{12}-A, were prepared by Charnell's method,[9] modified to include 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.

$Eu(OH)_2$ was prepared by a modification of Bärnighausen's method.[10] Approximately 0.8 g of europium metal (Ventron/Alfa, 99.9% purity) was added to 20 mL of 10 N NaOH. The lemon yellow $Eu(OH)_2$ which precipitated was washed repeatedly with ethanol and dried under vacuum.

Ion exchange was performed in the dark by flow methods—a saturated aqueous solution of $Eu(OH)_2$ was allowed to flow past the crystal at approximately 1.0 mm/s, at 25 °C, for 4.5 days. After the exchange, the crystal was sealed in its capillary under nitrogen. Microscopic examination indicated that the resulting clear colorless crystal had not been damaged by this procedure.

All manipulations, from the synthesis through the ion-exchange, were carried out under a pure nitrogen atmosphere using Kontes Airless-ware. All solvents were thoroughly deoxygenated before use. Subsequent diffraction intensities were collected at 23 (1) °C.

Chemical analysis for europium was not performed; that five Eu(II) ions are present per unit cell was established by occupancy refinement. This determination is expected to be entirely accurate because of the unusually large data set and the large scattering factor of europium for X-rays.

The space group *Pm*3*m* (no systematic absences) was used throughout this work for reasons discussed previously.[11,12] 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 ($K\alpha_1$, λ 0.709 30 Å; $K\alpha_2$, λ 0.713 59 Å). The cubic unit cell constant, as determined by least-squares refinement of 15 intense reflections for which $20° < 2\theta < 24°$, is 12.290 (2) Å.

Reflections from two intensity-equivalent regions of reciprocal space (hkl, $h \le k \le l$; lhk, $l \le h \le k$) were examined using the θ–2θ scan technique. Each reflection was scanned at a constant rate of 1.0° min^{-1} from 0.8° (in 2θ) 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. The intensities of three reflections in diverse regions of reciprocal space were recorded after every hundred reflections to monitor crystal and instrument stability. Only small, random fluctuations of these check reflections were noted during the course of data collection.

For each region of reciprocal space, the intensities of all lattice points for which $2\theta < 70°$ were recorded. Although few reflections were significantly greater than background for high 2θ values, this limit was selected to give a more complete data set.

The raw data for each region were corrected for Lorentz and polarization effects, including that due to incident beam monochromatization; the reduced intensities were merged; and the resultant estimated standard deviations were assigned to each averaged reflection by the computer program COMPARE.[13] Other details regarding data reduction have been discussed previously.[14] An absorption correction ($\mu = 4.6\ \text{mm}^{-1}$) was not applied because the crystal used was a very

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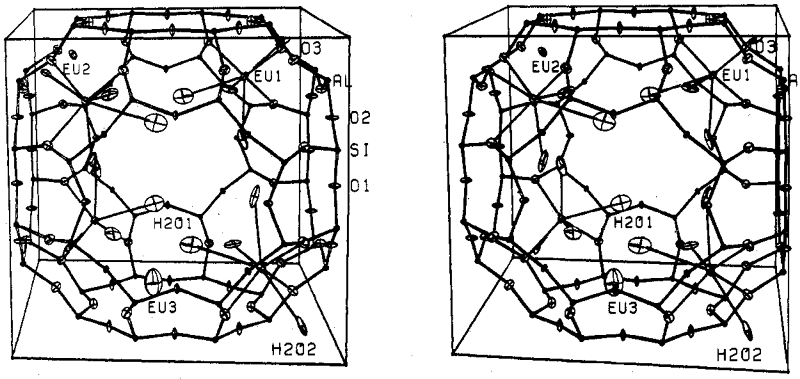

Figure 1. A stereoview of the hydrated Eu_5Na_2-A unit cell. Approximately 50% of the unit cells contain four ions at Eu(1) and no ions at Eu(2); the other 50% contain three at Eu(1) and one at Eu(2) as is shown. The water molecules at $H_2O(3)$ have not been drawn. Ellipsoids of 20% probability are used. The β_{23} parameter on O(2) was decreased by 1.5σ to produce a positive-definite thermal ellipsoid.

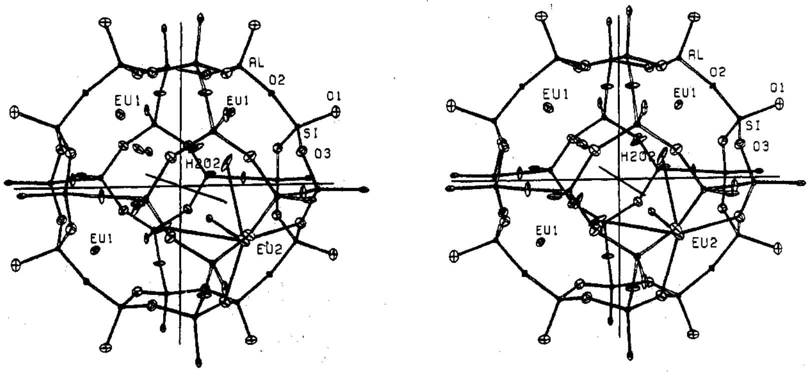

Figure 2. A stereoview of the hydrated Eu_5Na_2-A sodalite unit. Approximately 50% of the unit cells appear as in the figure; the other 50% contain eight water molecules at $H_2O(2)$ and no ions at Eu(2) in the sodalite unit. Other comments in the caption to Figure 1 apply here as well.

small cube; this correction in the similar case of dehydrated $Rb_{11}Na_1$-A ($\mu = 8.8$ mm^{-1}) had a negligible effect on the final structure.[15] Of the 886 unique pairs of reflections examined, only the 527 for which $I_o > 3\sigma(I_o)$ were used to solve and refine the structure. The crystal has a unit cell composition of $Eu_5Na_2Si_{12}Al_{12}O_{48}\cdot 21H_2O$ (additional water molecules may be present) and will be referred to subsequently as hydrated Eu_5Na_2-A.

Structure Determination

Full-matrix least-squares refinement of the structure was initiated using the atomic parameters of dehydrated $Eu_{5.75}Na_{0.5}$-A[2] for the atoms of the aluminosilicate framework: (Si,Al), O(1), O(2), and O(3). A probable europium position, Eu(1), was also included in this initial model (see Figure 1 to identify these positions). Anisotropic refinement of the framework atoms and isotropic refinement of Eu(1) converged to an R_1 index, $(\sum(F_o - |F_c||/\sum F_o)$, of 0.486 and a weighted R_2 index,$(\sum w(F_o - |F_c|)^2/\sum wF_o^2)^{1/2}$, of 0.417. The occupancy of the Eu(1) position, which was allowed to vary, converged at approximately four ions per unit cell.

A subsequent difference electron density function clearly revealed a europium ion in the sodalite unit at Eu(2). Inclusion of this position in least-squares refinement lowered the error indices to approximately 0.20. At this point an electron density difference function revealed the positions of Eu(3), $H_2O(1)$, and $H_2O(2)$ as peaks 2.6, 1.5, and 3.1 e Å^{-3} in height, respectively. These peak densities support the partial occupancies selected (Table I) for these 24-fold and 48-fold equipoints. Approximately three somewhat disordered water molecules at $H_2O(3)$ were subsequently located also.

Simultaneous occupancy, positional, and anisotropic thermal parameter refinement of Eu(1), Eu(2), Eu(3), $H_2O(1)$, and $H_2O(2)$ converged at the occupancies shown in the last column of Table I. By the assumption of stoichiometry, and the requirement that the structure be plausible, the occupancies of Eu(1), Eu(2), Eu(3), and $H_2O(1)$ were rounded to 3.5, 0.5, 1.0, and 10.5 ions or water oxygens per unit cell, respectively. Anisotropic refinement of all positions except $H_2O(3)$, which was refined isotropically, converged with the final error indices $R_1 = 0.120$ and $R_2 = 0.106$ at the fixed occupancies shown in Table I. Unlocated Na^+ ions and H_2O molecules contribute to these relatively high values. The structure is shown in Figures 1 and 2.

The goodness-of-fit, $(\sum w(F_o - |F_c|)^2/(m - s))^{1/2}$, is 5.30; the number of observations is 527; 50 variables were refined. All shifts in the final cycle of refinement were less than 10% of their corresponding esd's. The largest peak on the final difference Fourier function, whose estimated standard deviation at a general position is 0.20 e Å^{-3}, was 3.5 e Å^{-3} in height on the threefold axis at (0.30, 0.30, 0.30). When included in least squares, its occupancy refined to 0.9 (5) water molecule per unit cell; because this value was not significant and the *R* values were not affected, this position was not included in the final model. Nonetheless, this peak could represent 0.5 water molecule coordinated to Eu(2).

The two Na^+ ions per unit cell could not be located. They are likely to be associated with the remaining two unoccupied 8-rings per cell. If that is the case, locating them is impeded by the presence of the ion at Eu(3) because the Na^+ ions are likely to have coordinates nearly equivalent to those of Eu(3) by symmetry.

The possibility that the unit cell composition of this material is $Eu^{II}_3Eu^{III}_2Si_{12}Al_{12}O_{48}$, exclusive of water molecules, can nearly be dismissed. The insolubility of $Eu(OH)_3$ in aqueous solution, and the generally observed extreme reluctance of trivalent cations to enter the zeolite A lattice under ambient conditions, virtually ensures that no Eu(III) ions entered the zeolite during ion exchange. Also the extent of europium exchange for Na^+ has been observed to be variable, reaching levels of 5.75[2] and 5.5[16] ions per unit cell in previous experiments.

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 as supplementary material.

The full-matrix least-squares program[13] used minimized $\sum w(\Delta|F|)^2$; the weight (w) of an observation was the reciprocal square of $\sigma(F)$, its standard deviation. Atomic scattering factors[17] for Eu^{2+}, 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

Table I. Positional, Thermal,[a] and Occupancy Parameters for Hydrated Eu_5Na_2-A

	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor Fixed	Occupancy factor Varied
(Si,Al)	24(k)	0	1835 (3)	3740 (3)	15 (2)	11 (2)	9 (2)	0	0	4 (3)	1[c]	1
O(1)	12(h)	0	2303 (11)	$^1/_2$	68 (12)	35 (10)	9 (8)	0	0	0	1	1
O(2)	12(i)	0	2890 (7)	2890 (7)	80 (13)	12 (5)	12 (5)	0	0	36 (14)	1	1
O(3)	24(m)	1111 (6)	1111 (6)	3485 (9)	47 (5)	47 (5)	46 (8)	29 (14)	14 (10)	14 (10)	1	1
Eu(1)	8(g)	2268 (2)	2268 (2)	2268 (2)	39 (1)	39 (1)	39 (1)	25 (3)	25 (3)	25 (3)	0.437	0.41 (1)
Eu(2)	8(g)	1550 (16)	1550 (16)	1550 (16)	48 (9)	48 (9)	48 (9)	34 (23)	34 (23)	34 (23)	$^1/_{16}$	0.066 (2)
Eu(3)	24(m)	624 (57)	4377 (24)	4377 (24)	440 (139)	186 (31)	186 (31)	−34 (72)	−34 (72)	−132 (81)	$^1/_{24}$	0.040 (4)
$H_2O(1)$	48(n)	2413 (31)	2980 (38)	4465 (45)	37 (31)	147 (63)	333 (107)	−69 (86)	−144 (81)	24 (91)	0.22	0.24 (2)
$H_2O(2)$	24(m)	792 (33)	1141 (20)	1141 (20)	149 (55)	38 (16)	38 (16)	105 (40)	105 (40)	42 (41)	0.31	0.31 (4)
$H_2O(3)$	24(m)	3241 (86)	4435 (68)	4435 (68)	13 (6)[d]						$^3/_{24}$	

[a] Positional and anisotropic thermal parameters are given $\times 10^4$. 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, $\mu_i = 0.225a(\beta_{ii})^{1/2}$; a = 12.290 Å. [c] Occupancy for (Si) = $^1/_2$; occupancy for (Al) = $^1/_2$. [d] Isotropic thermal parameter in units of Å^2.

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

(Si,Al)-O(1)	1.656 (5)	Eu(2)-O(3)	2.50 (1)
(Si,Al)-O(2)	1.665 (3)	Eu(2)-$H_2O(2)$	2.96 (5)
(Si,Al)-O(3)	1.660 (3)	Eu(3)-O(1)	2.76 (3)
Eu(1)-O(3)	2.505 (10)	Eu(3)-O(2)	2.70 (5)
Eu(1)-$H_2O(1)$	2.84 (5)	O(3)···$H_2O(2)$	2.91 (4)
Eu(1)-$H_2O(2)$	2.67 (4)		
O(1)-(Si,Al)-O(2)	108.3 (6)	O(3)-Eu(1)-$H_2O(2)$	68.3 (8)
O(1)-(Si,Al)-O(3)	111.4 (4)	O(3)-Eu(1)-$H_2O(2)$	79.4 (5)
O(2)-(Si,Al)-O(3)	107.4 (5)	$H_2O(1)$-Eu(1)-$H_2O(1)$	68 (2)
O(3)-(Si,Al)-O(3)	110.8 (8)	O(3)-Eu(2)-O(3)	111 (1)
(Si,Al)-O(1)-(Si,Al)	138.9 (9)	O(3)-Eu(2)-$H_2O(2)$	84.7 (8)
(Si,Al)-O(2)-(Si,Al)	167.7 (9)	$H_2O(2)$-Eu(2)-$H_2O(2)$	69 (1)
(Si,Al)-O(3)-(Si,Al)	147.7 (8)	O(1)-Eu(3)-O(1)	115.6 (8)
O(3)-Eu(1)-O(3)	110.8 (6)	O(1)-Eu(3)-O(2)	59 (1)
O(3)-Eu(1)-$H_2O(1)$	69.0 (9)		

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

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

Atom	Dev, Å	Atom	Dev, Å
Eu(1)	0.78	$H_2O(1)$	2.94
Eu(2)	−0.75	$H_2O(2)$	−1.87

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

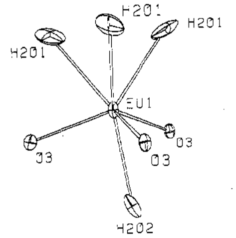

Figure 3. C_{3v}-capped trigonal-prismatic europium(II). The coordination environment of Eu(1) in hydrated Eu_5Na_2-A is shown with ellipsoids of 20% probability.

modified to account for the real component of the anomalous dispersion correction.[18]

Discussion

Within the large cavity of hydrated Eu_5Na_2-A, 3.5 Eu(II) ions per unit cell at Eu(1) are distributed over the eight positions of the Eu(1) equipoint, each 0.78 Å from a [111] plane at O(3). Each ion at Eu(1) is seven-coordinate. Its coordination sphere consists of three O(3) oxide ions of the 6-rings of the zeolite framework (Eu(1)–O(3) = 2.50 (1) Å) and four water molecules. Three, at $H_2O(1)$, are equivalent (Eu(1)–$H_2O(1)$ = 2.84(5) Å) and lie deep within the large cavity at a general equipoint, 2.94 Å from the O(3) plane. The seventh coordination site is occupied by the water molecule at $H_2O(2)$ (Eu(1)–$H_2O(2)$ = 2.67 (4) Å), which lies on a mirror plane near a threefold axis within the sodalite unit. The Eu(II)–H_2O bond lengths in $EuCl_2{\cdot}2H_2O$ range from 2.69 (2) to 2.74 (2) Å.[19] Figure 3 shows the seven-coordination about Eu(1).

An axially capped (C_{3v}) trigonal prism, an idealized polyhedron formed by the addition of a vertex to one triangular face of a trigonal prism, is the closest representation of the geometry about the europium ions at Eu(1). The three water molecules at $H_2O(1)$ are nearly eclipsed with respect to the three coordinating oxide ions at O(3). Figure 4 clearly shows the distortions from this idealized geometry; the water molecules at $H_2O(1)$ are rotated 16° from an eclipsed geometry with respect to the O(3) oxides. Perhaps the capping ligand at $H_2O(2)$ is displaced (by a small amount) from the threefold axis in order to hydrogen bond at 2.91 (4) Å to an O(3) oxide ion.

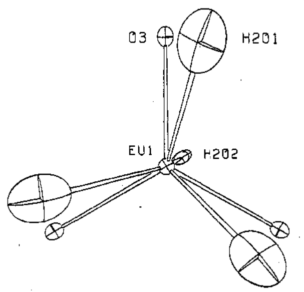

Figure 4. A view of the Eu(1) coordination sphere along the threefold axis of the unit cell showing distortions from an ideal C_{3v}-capped trigonal prism. Ellipsoids of 20% probability are used.

This appears to be the first report of C_{3v}-capped trigonal-prismatic coordination about any ion. Clearly the geometry of the zeolite lattice, particularly that of the 6-ring, has facilitated its occurrence. The Eu(II) ion at Eu(1) has moved into the large cavity to coordinate to three water molecules so that all six of the angles at Eu(1) involving $H_2O(1)$ to itself or $H_2O(1)$ to O(3) are approximately 69°. Sufficient solid angle remains through the 6-ring for only one additional H_2O ligand. Possibly in order to hydrogen bond to O(3) ions and to each other, the $H_2O(1)$ molecules have not positioned themselves differently about the threefold axis where they might have completed an alternative seven-coordinate polyhedron, a distorted monocapped octahedron. Although the angle is not optimal, a hydrogen-bonding interaction between the water molecules at $H_2O(1)$ and the framework O(3) oxide ions is possible with the distorted trigonal-prismatic geometry ($H_2O(1)$–O(3) = 3.05 Å).

Seven-coordination and eight-coordination have been reported previously for europium(II) in single-crystal structure determinations. Eu(II) is seven-coordinate in the monoclinic form of EuI_2.[20] Its coordination geometry is best approximated by the tetragonal base–trigonal base structural unit with angles about Eu(II) which average to 80.3°. The same coordination has been found in the structure of $YbCl_2$.[21] In europium dichloride dihydrate, each Eu(II) ion is coordinated by four Cl^- ions and four water molecules[19] which form a distorted archimedian antiprism.

In the sodalite unit along the threefold axis, 0.75 Å from the O(3) plane, 0.5 Eu(II) ion per unit cell at Eu(2) is found. This ion is either six- or seven-coordinate; although the positions for only six ligand atoms have been established, the possibility of seven-coordination at Eu(2) cannot be dismissed. It remains possible that an unlocated water molecule in the large cavity coordinates to Eu(2) through a 6-ring just as an $H_2O(2)$ molecule coordinates to Eu(1). The occupancy of this position would be only 0.5 oxygen atom per unit cell and would be located at a position nearly related by symmetry to Eu(1). The location of such a water oxygen is judged to be beyond the resolution of this work, even though a small Fourier peak was found at just this position (vide supra).

The ion at Eu(2) is bound to three O(3) ions at 2.50 (1) Å and to three $H_2O(2)$ oxygen atoms at 2.96 (5) Å. By symmetry, the O(3)–Eu(2)–$H_2O(2)$ planes bisect the O(3)′–Eu(2)–O(3)′ angle (the O(3)′ positions are related to O(3) by the threefold axis operation). Therefore, assuming that Eu(2) is six-coordinate, the coordination about Eu(2) is trigonally distorted octahedral (see Figure 5), further distorted because Eu(2) lies closer to the O(3)'s than to the $H_2O(2)$'s. If Eu(2) is seven-coordinate, the coordination is best described as trigonally distorted C_{3v}-capped octahedral.

The occupancies at Eu(1), $H_2O(1)$, Eu(2), and $H_2O(2)$, at 3.5, 10.5, 0.5, and 7.5 per unit cell, respectively, indicate that all unit cells are not identical. Within approximately 50% of the large cavities, four europium ions at Eu(1) are found, while the other half of the large cavities contain only three. A complementary half of the sodalite units contain eight molecules at $H_2O(2)$ and no ions at Eu(2), while the other half contain seven molecules at $H_2O(2)$ and one Eu(2) ion, respectively. On the basis of previous structural results on zeolite A,[3] all large cavities or sodalite units can be expected to be associated with four Eu(II) ions arranged tetrahedrally with respect to the eight 6-rings. In approximately half of the unit cells, then, four threefold-axis Eu(II) ions are on the large cavity side of the 6-rings; in the other half, three are on the large cavity side and one lies on the other (sodalite cavity) side of the 6-rings.

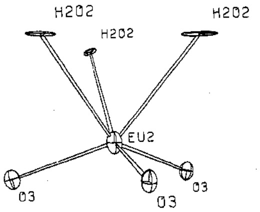

Figure 5. The coordination environment of Eu(2) in hydrated Eu_5Na_2-A shown using ellipsoids of 20% probability. As discussed in the text, this ion may be seven-coordinate.

Hydrogen bonding in the sodalite unit of Eu_5Na_2-A is extensive. Each water molecule at $H_2O(2)$ lies near a vertex of a cube and participates in two equivalent hydrogen bonds, each to a framework O(3); $H_2O(2)$–O(3) = 2.91(4) Å. The $H_2O(2)$–$H_2O(2)$ separation is 3.35 Å. In the half of the unit cells which contain eight molecules at $H_2O(2)$, an approximate cube is completed, while in the other half only seven corners are occupied. A similar cubic arrangement of eight water molecules was found in the sodalite unit of hydrated K_{12}-A.[22]

All of the molecules at $H_2O(2)$ should not be equivalent, because they are of three chemically different types: those bound to Eu(1), those bound to Eu(2), and those involved only in hydrogen bonding to the framework and perhaps to each other. However, the differences are apparently small, perhaps because all $H_2O(2)$ molecules form strong equivalent hydrogen bonds to the framework. This position could not be separated into several in least-squares refinement. Furthermore the anisotropic thermal parameters at $H_2O(2)$ are not unusually large, indicating little positional disorder.

The remaining Eu(II) ion in hydrated Eu_5Na_2-A, at Eu(3), lies on a mirror plane in the large cavity near the plane of an 8-ring. It approaches two 8-ring oxide ions at O(1) at 2.76 (3) Å and one at O(2) at 2.70 (5) Å, somewhat longer than the framework approaches made by the europium ions at Eu(1) and Eu(2). These longer bonds are indicative of the less favorable coordination provided by an 8-ring site as compared to that of a 6-ring. Although water molecules associated with Eu(3) could not be located, this is not unusual because they are likely to be nonequivalent and to have small occupancy parameters.

The $H_2O(3)$ position represents approximately three disordered water molecules per unit cell. These are apparently involved in hydrogen bonding to other unlocated water molecules within the large cavity.

The Eu(1)–O(3) and Eu(2)–O(3) bonds in hydrated Eu_5Na_2-A are more than 0.1 Å longer than the corresponding bonds in dehydrated $Eu_{5.75}Na_{0.5}$-A,[2] where the europium ions are three-coordinate. This simply indicates the expected dependence of ionic radius on coordination number. An effective ionic radius of 1.20 Å is obtained for seven-coordinate Eu(II) using Shannon's tables of coordination-number-dependent ionic radii.[23] The sum of the appropriate ionic radii (using a value of 1.32 Å for O^{2-})[24] is then 2.52 Å, in good agreement with the observed Eu(1)–O(3) and Eu(2)–O(3) bond lengths. Water molecules engage in somewhat weaker interactions with Eu(II) ions relative to framework oxides, as indicated by the longer Eu(II)–H_2O bonds. The particularly long Eu(2)–$H_2O(2)$ bond may result in part from the strong hydrogen-bonding interactions between $H_2O(2)$ water molecules and framework O(3) oxide ions.

Only the angles O(3)–Eu(1)–$H_2O(2)$ and O(3)–Eu(2)–$H_2O(2)$, at 79.4 (5) and 84.7 (8)°, respectively, are near the ideal value of 77° which results when all atoms of a seven-coordinate complex are placed at equal distances from the metal ion so that all adjacent pairs of atoms make equal angles at the metal.[25] The O(3)–Eu(1)–O(3) and O(3)–Eu(2)–O(3) angles at 111° are considerably larger as a result of 6-ring constraints. All remaining angles about both Eu(1) and Eu(2) are smaller, nearly identical at 69°, somewhat less than the average value found in eight-coordinate square-antiprismatic complexes.[26] This suggests that the zeolite framework, which requires that three coordination angles of an ion associated with a 6-ring not be too much less than 120°, has kept the coordination number of these ions from being eight, or more.

Hydrated Eu_5Na_2-A has a remarkable structure. In no previous zeolite A structure has such an elaborate and well-ordered bonding network between cations, ligands, and the framework been found. The molecules at $H_2O(2)$ in the sodalite unit form a well-ordered hydrogen-bonded structure and, in addition and in different ways, participate in the coordination spheres of both Eu(1) and Eu(2).

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Supplementary Material Available: Listing of the observed and calculated structure factors, Supplementary Table I (4 pages). Ordering information is given on any current masthead page.

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Allylmanganese Phosphine and Phosphite Chemistry. Synthesis, Chemistry, and Catalytic Properties[1]

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A new family of compounds derived from η^3-$C_3H_5Mn(CO)_4$ by partial substitution of CO by trialkyl phosphites and trialkylphosphines has been synthesized and its catalytic chemistry explored. The disubstituted compounds η^3-$C_3H_5Mn(CO)_2(PR_3)_2$, with R = OCH_3, O-*i*-C_3H_7, and C_2H_5, catalyzed the hydrogenation of alkenes with rates that increased as the steric bulk of the phosphorus ligand increased and without detectable catalyst decomposition. These allylmanganese species selectively complexed acetylenes over olefins under hydrogenation conditions and thus they selectively hydrogenate an acetylene to an olefin. The trisubstituted compound η^3-$C_3H_5Mn(CO)[P(OCH_3)_3]_3$ was a rapid alkene hydrogenation catalyst precursor which underwent a rapid competitive loss of the allyl group as propene and concomitant catalyst death. The compound η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ reacted with CH_3SO_3H and with CF_3SO_3H through a formal displacement of the η^3-allyl by an alkanesulfonato group to give $(CH_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ and $(CF_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$, respectively. The methanesulfonato complex was a catalyst precursor for the hydrogenation of 1-hexene, although less active than the corresponding allylmanganese complex. Unlike the formally analogous η^3-$C_3H_5Co[P(OR)_3]_3$ compounds, none of the above catalyzed the hydrogenation of benzene. Reaction of η^3-$C_3H_5Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$ with CF_3SO_3H in the presence of dienes gave $(\text{diene})Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2{}^+CF_3SO_3{}^-$ compounds. The norbornadiene derivative was obtained in good yield whereas only a low yield of the 1,5-cyclooctadiene analogue was isolated, the major product being $(CF_3SO_3)Mn(CO)_2[P(O\text{-}i\text{-}C_3H_7)_3]_2$. This new manganese chemistry appears to provide the first examples of a Mn(I)–Mn(III) couple in coordination catalysis.

Introduction

Designed control of the chemistry of a coordination or organometallic complex can be achieved by ligand modification. A ligand combination set that we have found especially effective for oxidative-addition reactions is the π-allyl ligand with either phosphine or phosphite ligands. The latter increase the electron density on the metal atom and thereby enhance the potential for an oxidative addition while the allyl ligand through generally facile π–σ transformations can provide the coordinately unsaturated intermediate. The efficacy of this ligand combination set is illustrated in the chemistry of the η^3-$C_3H_5Co[P(OR)_3]_3$ and η^3-$C_3H_5Co(PR_3)_3$ complexes which

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