

issue.

- (6) The more general use of 1,2-carbonyl addition reactions to convert nitrocyclohexadienones to nitrocyclohexadienols has not escaped our attention. The method is presently being employed as a useful and often the preferred method of ipso adduct synthesis.
- (7) The major by-products were nitroxylenols formed by thermal rearrangement of the dienone reactant.⁵
- (8) Ratio reported is that obtained after correction for ¹³C and the small amount of residual protium at C-2 and C-6 of the labeled phenol.
- (9) If $k_o \neq k_o'$, the equation shown takes the following form

$$k_o/k_{\text{ipso}} = \{(2-d_2)/(2-d_1) - k_o/k_o'\}$$

- (10) Near equilibration may be taken to imply that $k_o/k_{\text{ipso}} < 0.1$.
- (11) This result might have been predicted on the basis of Hahn's report that strong acid solvolysis of a crude mixture containing 87% 3-isopropyl-4-methyl-4-nitrocyclohexadienyl acetate and 13% 4-isopropyl-3-methyl-4-nitrocyclohexadienyl acetate gave 10% 3-isopropyl-2-methylnitrobenzene and 90% *o*-nitrotoluene (via nitrodeisopropylation): R. C. Hahn, H. Shosenji, and D. L. Strack, *ACS Symp. Ser.*, **No. 22**, 95 (1975).
- (12) C. L. Perrin, *J. Am. Chem. Soc.*, **99**, 5516 (1977).
- (13) T. H. Brown and M. Karplus, *J. Chem. Phys.*, **46**, 870 (1967).

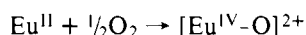
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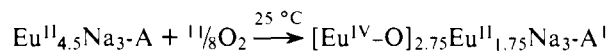
Europium(IV), a New Oxidation State for Europium. Crystal Structure of Dehydrated Europium(II)-Exchanged Sodium Zeolite A, Eu_{4.5}Na₃-A, Partially Oxidized by Oxygen

Sir:

Oxygen gas at a pressure of 1 atm was sorbed into a single crystal of vacuum-dehydrated europium(II)-exchanged zeolite A, Eu_{4.5}Na₃-A,¹ at 25 °C. As a result, ~2.75 previously three-coordinate near-planar Eu(II) ions per unit cell became four coordinate, according to a crystal structure determination, having added one oxide ion each to their coordination spheres. These oxide ions extend into the sodalite cavities² where they participate in no additional coordination interactions. They are therefore one coordinate. The net reaction



has occurred 2.75 times per unit cell to give a product in which the formal oxidation state of 2.75 europium ions is +4. The overall reaction per unit cell is



It was anticipated that the exposure of oxygen to dehydrated Eu(II)-exchanged zeolite A would result either in (1) no reaction, (2) the formation of a dioxygen complex which would be stable within the zeolite, or (3) a reaction to form Eu(III) ions bridged by oxides in the sodalite unit. The oxidation of europium to the tetravalent state, resulting from the coordination of a single nonbridging oxide ion, was unexpected.

Apparently a structure involving Eu(III) and bridging oxide ions has not occurred because of the reluctance of the europium ions to leave their sites of close approach to the zeolite framework. The rigid structure and relatively uniform charge distribution of the oxide ions of the zeolite framework constrains the europium ions to positions which are relatively far apart.

The exposure of dehydrated Eu(II)-exchanged zeolite A to an even stronger oxidizing agent, chlorine gas, leads to a five-coordinate trigonal-bipyramidal europium(IV) chloride complex containing two chloride ions coordinated axially to each Eu(IV) ion. This structure is reported in the following communication.³

A single crystal of sodium zeolite 4A, Na₁₂-A,¹ 0.085 mm

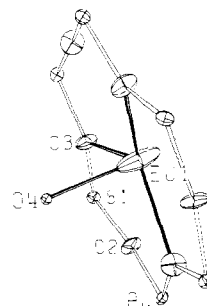


Figure 1. The four-coordinate Eu(IV) complex. The structure shown occurs ~2.75 times per unit cell. Selected bond lengths in angstroms are Eu(1)-O(3) = 2.284 (9) and Eu(1)-O(4) = 2.13 (4); some bond angles are O(3)-Eu(1)-O(3) = 118.4 (7)° and O(3)-Eu(1)-O(4) = 82.7 (3)°. Ellipsoids of 20% probability are shown.

on an edge, was lodged in a fine glass capillary. Lemon yellow Eu(OH)₂ was synthesized by a modification of Bärnighausens' method⁴ under anoxic conditions. Ion exchange proceeded for 4 days in the dark under a nitrogen atmosphere by allowing a saturated aqueous solution of Eu(OH)₂ to flow past the crystal at ~1.0 mm/s. The colorless crystal was then dehydrated for 48 h at 400 °C and 5 × 10⁻⁶ Torr. Microscopic examination showed the crystal to be undamaged; it had developed the bright orange color characteristic of dehydrated Eu(II)-exchanged zeolite A. Finally, the crystal was treated at 25 °C with 760 Torr of zeolitically dried high purity oxygen (99.99%) for 1 h. The capillary containing the crystal was then removed from the vacuum line by torch under 700 Torr of oxygen.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously;^{2a} $a = 12.238$ (2) Å at 23 °C. The structure was solved using the 343 unique observed ($I_o > 3\sigma(I_o)$; $2\theta < 70^\circ$) reflections collected by counter methods using a fully automated Syntex P1 diffractometer with monochromatic Mo K α radiation ($K\alpha_1$, $\lambda = 0.70930$ Å; $K\alpha_2$, $\lambda = 0.71359$ Å) and a pulse-height analyzer. Other experimental details including data reduction are the same as previously presented.⁵ The value of x in the formula of the unit cell, Eu _{x} Na_{12-2 x} Si₁₂Al₁₂O₄₈, exclusive of oxide ions at O(4), was determined to be 4.5 by refinement of the occupancies of europium positions.

Full-matrix least-squares refinement⁶ using anisotropic temperature factors for all positions except O(4) and Na, which were refined isotropically, converged to the error indices, $R_1 = (\sum |F_o - |F_c|| / \sum F_o) = 0.097$ and $R_2 = (\sum w(F_o - |F_c|)^2 / \sum wF_o^2)^{1/2} = 0.095$ at the fixed occupancies shown in Table I. Simultaneous positional, occupancy, and thermal parameter refinement of the Eu(1), Eu(2), Eu(3), O(4), and Na positions led to the occupancy values given in the next to the last column of Table I with nearly no change in the error indices. Decreasing the occupancy of Eu(1) to 2.5 ions per unit cell or increasing it to 3.0, increased R_1 by 0.0005 and 0.004, respectively, as all other parameters varied to convergence. As a result the occupancy of Eu(1) was fixed at 2.75 ions per unit cell. The overdetermination ratio is 9.8 for the 35 parameters varied in least squares.

The Eu(IV) ions are four coordinate, as can be seen in Figure 1. They lie near the planes of 6-rings and coordinate to three O(3) oxide ions of the zeolite framework and to one threefold axis oxide ion, O(4), which extends into the sodalite unit. Each oxide ion at O(4) coordinates only to one Eu(IV) ion at Eu(1). The unusual geometry of the four-coordinate Eu(IV) complex can best be described as a slightly inverted trigonal pyramid.

The Eu(1)-O(3) bond distance, 2.28 Å, is almost 0.1 Å less than the threefold-axis Eu(II)-O(3) bond found in dehydrated Eu_{11.75}-A.⁷ The Eu(1)-O(4) bond at 2.14 Å is very near the sum of the appropriate ionic radii, 2.17 Å, assuming an ionic

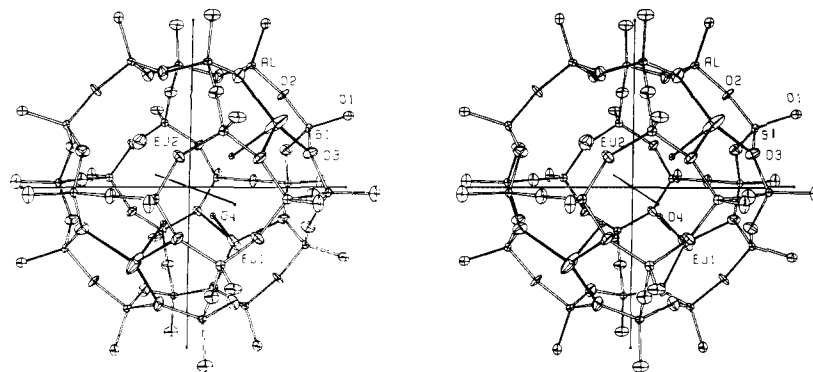


Figure 2. A stereoview of approximately three-quarters of the sodalite units of $[\text{Eu}^{\text{IV}}\text{-O}]_{2.75}\text{Eu}^{\text{II}}_{1.75}\text{Na}_3\text{-A}$ is shown. The least-squares results indicate that the remaining one-quarter of the sodalite units contain only two $\text{Eu}^{\text{IV}}\text{-O}$ species and two Eu^{II} ions at $\text{Eu}(2)$. Selected bond lengths in angstroms are $(\text{Si,Al})\text{-O}(1) = 1.641$ (5), $(\text{Si,Al})\text{-O}(2) = 1.643$ (4), $(\text{Si,Al})\text{-O}(3) = 1.675$ (4), and $\text{Eu}(2)\text{-O}(3) = 2.57$ (1). Ellipsoids of 20% probability are shown.

Table I. Positional, Thermal,^a and Occupancy Parameters for $[\text{Eu}^{\text{IV}}\text{-O}]_{2.75}\text{Eu}^{\text{II}}_{1.75}\text{Na}_3\text{-A}$

	Wyckoff position	x	y	z	β_{ij} ^b or B_{iso}					Occupancy factor		
					β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Varied	Fixed
(Si,Al)	24 (k)	0	1832 (3)	3722 (3)	33 (3)	36 (3)	20 (3)	0	0	10 (5)	1 ^c	1 ^c
O(1)	12 (h)	0	2237 (11)	1/2	110 (17)	38 (11)	50 (13)	0	0	0	1	1
O(2)	12 (i)	0	2866 (9)	2866 (9)	89 (15)	55 (8)	55 (8)	0	0	87 (21)	1	1
O(3)	24 (m)	1120 (6)	1120 (6)	3387 (8)	55 (5)	55 (5)	90 (10)	53 (14)	22 (12)	22 (12)	1	1
Eu(1)	8 (g)	2012 (5)	2012 (5)	2012 (5)	149 (5)	149 (5)	149 (5)	203 (11)	203 (11)	203 (11)	0.33 (1)	0.344
Eu(2)	8 (g)	1306 (8)	1306 (8)	1306 (8)	110 (7)	110 (7)	110 (7)	-22 (16)	-22 (16)	-22 (16)	0.15 (1)	0.156
Eu(3)	12 (j)	1888 (91)	1888 (91)	1/2	610 (148)	610 (148)	156 (88)	443 (393)	0	0	0.038 (5)	0.042
O(4)	8 (g)	1012 (21)	1012 (21)	1012 (21)	0.8 (8)						0.30 (4)	0.344
Na	12 (i)	0	4215 (84)	4215 (84)	9 (5)						0.13 (5)	0.083

^a Positional and anisotropic parameters are given $\times 10^4$. 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 Root-mean-square displacements can be calculated from β_{ij} values using the formula, $\mu_i = 0.225a(\beta_{ij})^{1/2}$, where $a = 12.238$ Å. ^c Occupancy for (Si) = $1/2$; occupancy for (Al) = $1/2$.

Table II. Fourth Ionization Potentials ($\text{M}^{3+} \rightarrow \text{M}^{4+} + \text{e}^-$) in Volts for the Lanthanides and Hafnium^a

Element	Atomic no.	Ionization potential	Element	Atomic no.	Ionization potential
Ce ^b	58	36.758	Dy ^c	66	41.47
Pr ^c	59	38.98	Ho	67	42.5
Nd ^c	60	40.41	Er	68	42.65
Pm	61	41.1	Tm	69	42.69
Sm	62	41.4	Yb	70	43.74
Eu	63	42.6	Lu	71	45.19
Gd	64	44.0	Hf ^b	72	33.33
Tb ^c	65	39.79			

^a Reference 11. ^b The tetravalent state is stable in solution and in solids. ^c The tetravalent state has only been observed in solids.¹²

radius of 0.85 Å for Eu^{IV} ^{8,9} and 1.32 Å for O^{2-} .⁹ The europium ion at $\text{Eu}(2)$ has not been oxidized; it remains in the divalent state. It is trigonally coordinated to three $\text{O}(3)$'s of a 6-ring at 2.57 Å. Another Eu^{II} ion, at $\text{Eu}(3)$, is located opposite a 4-ring at a position very similar to that found for a Eu^{II} ion in dehydrated $\text{Eu}^{\text{II}}_{5.75}\text{-A}$.⁷ It approaches two $\text{O}(3)$ and two $\text{O}(1)$ oxide ions at approximately equal distances: $\text{Eu}(3)\text{-O}(3) = 2.38$ Å, and $\text{Eu}(3)\text{-O}(1) = 2.35$ Å. These are typical $\text{Eu}^{\text{II}}\text{-O}$ coordination distances.⁷ The large thermal parameters associated with $\text{Eu}(3)$ may indicate some positional disorder.

Finally, one sodium ion is located in the plane of the 8-ring 2.60 (6) Å from two $\text{O}(1)$ oxide ions and 2.3 (1) Å from one $\text{O}(2)$ oxide ion. The remaining two sodium ions could not be found, but they are probably also associated with the 8-rings.

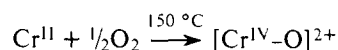
It is interesting to note that the oxide ions at $\text{O}(4)$ are located in the sodalite unit, while the Eu^{IV} ions extend into the large cavity by a small amount, 0.29 Å. This means that the coordi-

ination about Eu^{IV} deviates from trigonal pyramidal in an unusual sense—the $\text{O}(4)\text{-Eu}^{\text{IV}}\text{-O}(3)$ angles are acute. If the $\text{O}(4)$ oxide ions were located on the large cavity side of the 6-ring, more conventional coordination, between trigonal pyramidal and tetrahedral, would have been possible. It appears that these unusual one-coordinate oxide ions at $\text{O}(4)$ are stabilized to some extent by the presence of one or two Eu^{II} ions at $\text{Eu}(2)$ on the opposite side of the sodalite unit, even though the $\text{Eu}(2)\text{-O}(4)$ distance is 4.03 Å (see Figure 2). Strong evidence for such stabilization comes from the 2.57-Å $\text{Eu}(2)\text{-O}(3)$ bond, which is 0.14 Å longer than a similar $\text{Eu}^{\text{II}}\text{-O}(3)$ bond in the structure of dehydrated $\text{Eu}^{\text{II}}_{5.75}\text{-A}$.⁷ If the $\text{O}(4)$ oxide ions were located in the large cavity, they could not be stabilized in this way.

Upon exposure to oxygen, there is little change in the color of the crystal, presumably because the oxidation to Eu^{IV} is not complete. The yellow-orange color probably arises from the ~ 1.25 Eu^{II} ions per unit cell at $\text{Eu}(2)$, and probably involves an $f \rightarrow d$ transition.^{7,10}

Table II shows that the fourth ionization potentials of the lanthanides are relatively constant and, in more detail, relatively smooth functions of atomic number. The fourth ionization potential of europium is only ~ 1 V higher than those of other lanthanides whose +4 state is known in the solid. Therefore it is reasonable that Eu(IV) also has been prepared and stabilized in the solid state.

A reaction similar to that reported here for Eu(II)-exchanged zeolite A occurs when O₂ is sorbed into dehydrated Cr(II)-exchanged zeolite A at 150 °C. Kellerman and Klier¹³ have concluded from reflectance spectroscopy and magnetic susceptibility measurements that the previously three-coordinate divalent chromium ion is oxidized to the tetravalent state, where it is tetrahedrally coordinated to three O(3) ions and a single oxide ion from the sorbed O₂, according to the reaction



The fourth ionization potential for chromium is 49.1 eV,¹⁴ greater than that of europium, and greater than that of any element listed in Table II; yet Cr^{II} can be oxidized by O₂ to Cr^{IV} at 6-ring sites in zeolite A.¹³ This indicates that the intrazeolitic reaction $\text{M}^{\text{II}} + \frac{1}{2}\text{O}_2 \rightarrow \text{M}^{\text{IV}}\text{-O}$ should occur with any lanthanide, perhaps including lanthanum whose fourth ionization potential is 49.95 eV.¹¹ In particular, this indicates that the europium ions in EuO²⁺ at Eu(1)) are Eu^{IV}, although the determination of their electronic structure, and therefore their oxidation state, remains to be done.

Trivalent lanthanide ion exchanged zeolites X and Y are widely used to prepare high-octane liquid fuel from crude oil. Perhaps redox processes involving the M^{IV} state are important in the preparation and function of these catalysts.

Acknowledgments. This work was supported by the National Science Foundation, Grant No. CHE76-81586. We are indebted to the University of Hawaii Computing Center.

Supplementary Material Available: Listing of the observed and calculated structure factors (Supplementary Table 1, 3 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) This nomenclature refers to the contents of the unit cell. For example, Eu_{4.5}Na₃-A represents Eu_{4.5}Na₃Si₁₂Al₁₂O₄₈, exclusive of guest species which may be present in the zeolite, such as water.
- (2) 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); (c) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).
- (3) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, following paper in this issue.
- (4) H. Bärnighausen, *Z. Anorg. Allg. Chem.*, **342**, 233 (1966).
- (5) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 1112 (1977).
- (6) 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.
- (7) The complete unit cell formula is Eu_{6-x}Na_{2x}Si₁₂Al₁₂O₄₈, 0 ≤ x ≤ 0.5: R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 7059 (1977).
- (8) This radius was obtained by extrapolation and by comparison with Ce(III) and Ce(IV).
- (9) "Handbook of Chemistry and Physics", 55th ed, The Chemical Rubber Co., Cleveland, Ohio, 1974, p F190.
- (10) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals", Wiley, New York, N.Y., 1968, pp 178, 179.
- (11) W. C. Martin, L. Hagan, J. Reader, and J. Sugar, *J. Phys. Chem. Ref. Data*, **3**, 771 (1974).
- (12) T. Moeller, *J. Chem. Educ.*, **47**, 417 (1970).
- (13) R. Kellerman and K. Klier in "Molecular Sieves—II", J. R. Katzer, Ed., American Chemical Society, Washington, D.C., 1977, pp 120–131.
- (14) W. J. Lotz, *J. Opt. Soc. Am.*, **57**, 873 (1967).

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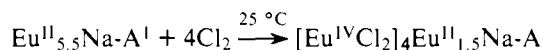
Five-Coordinate Europium(IV) and Zero-Coordinate Europium(II). Crystal Structure of Dehydrated Near-Fully Europium(II)-Exchanged Zeolite A, Eu_{5.5}Na-A, Partially Oxidized by Chlorine

Sir:

Chlorine gas at 220 Torr was sorbed into a single crystal of vacuum-dehydrated europium(II)-exchanged zeolite A, Eu_{5.5}Na-A,¹ at 25 °C. A subsequent determination of the crystal structure showed that four previously three-coordinate near-planar Eu(II) ions per unit cell had become five-coordinate, having added two chloride ions axially to their coordination spheres. One chloride ion extends into the large cavity, and the other is in the sodalite unit;² both coordinate to europium at very short distances. It follows that the net reaction



has occurred four times per unit cell. The overall reaction per unit cell is



The oxidation is not complete; 1.5 europium ions per unit cell remain in the divalent state. Surprisingly, one Eu(II) ion per unit cell is located on a fourfold axis near the center of an 8-ring, but off its plane. Although this Eu(II) ion does not appear to occupy a single well-defined site, it clearly lies at a position of zero coordination—its closest approach to the 8-ring oxide ions exceeds the sum of the appropriate ionic radii by >1.0 Å (see ref 3 for a complete discussion of the criterion used to define zero coordination).

This is the second zeolite A structure to contain europium in the tetravalent oxidation state. The sorption of oxygen on dehydrated Eu(II)-exchanged zeolite A leads to a four-coordinate Eu(IV) complex, and is reported in the preceding communication.⁴

A single crystal of sodium zeolite A, Na₁₂-A¹, 0.085 mm on an edge, was lodged in a fine glass capillary. A saturated aqueous solution of Eu(OH)₂, synthesized by a modification of Bärnighausens' method,⁵ was allowed to flow past the crystal at a rate of ~ 1.0 mm/s for 5 days. Ion exchange was performed in the dark in an oxygen-free nitrogen atmosphere. The crystal, whose appearance was not altered by this exchange procedure, was then dehydrated for 48 h at 400 °C and 5×10^{-6} Torr. Microscopic examination indicated that the crystal was still clear and undamaged, and had developed the bright orange color characteristic of dehydrated Eu(II)-exchanged zeolite A.

The crystal was then treated at 25 °C with 220 Torr of zeolitically dried chlorine gas, and immediately became colorless. After 1 h, the crystal, still in its chlorine atmosphere,

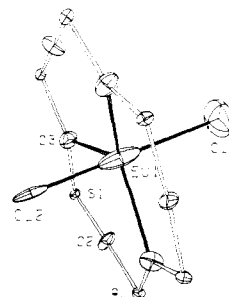


Figure 1. A view of the trigonal-bipyramidal Eu(IV) complex. This structure occurs four times per unit cell. Selected bond lengths in angstroms are Eu(1)-O(3) = 2.31 (1), Eu(1)-Cl(1) = 2.52 (4), and Eu(1)-Cl(2) = 2.06 (3); some bond angles are O(3)-Eu(1)-O(3) = 118.3 (8)°, Cl(1)-Eu(1)-O(3) = 97.5 (8)°, and Cl(2)-Eu(1)-O(3) = 82.5 (8)°. Ellipsoids of 20% probability are shown.