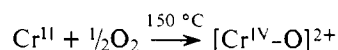Table II shows that the fourth ionization potentials of the lanthanides are relatively constant and, in more detail, relatively smooth functions of atomic number. The fourth ionization potential of europium is only ~1 V higher than those of other lanthanides whose +4 state is known in the solid. Therefore 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 O_2 is sorbed into dehydrated Cr(II)-exchanged zeolite A at 150 °C. Kellerman and Klier[13] 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 O_2, according to the reaction

$$Cr^{II} + \frac{1}{2}O_2 \xrightarrow{150\ °C} [Cr^{IV}-O]^{2+}$$

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 O_2 to Cr^{IV} at 6-ring sites in zeolite A.[13] This indicates that the intrazeolitic reaction $M^{II} + \frac{1}{2}O_2 \rightarrow M^{IV}-O$ 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 EuO^{2+} 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.

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, $Eu_{4.5}Na_3$-A represents $Eu_{4.5}Na_3Si_{12}Al_{12}O_{48}$, 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 $Eu_{6-x}Na_{2x}Si_{12}Al_{12}O_{48}$, $0 \leq x \leq 0.5$; 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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Received September 26, 1977

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

$$Eu^{II} + Cl_2 \rightarrow [Eu^{IV}Cl_2]^{2+}$$

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

$$Eu^{II}_{5.5}Na\text{-}A^1 + 4Cl_2 \xrightarrow{25\ °C} [Eu^{IV}Cl_2]_4Eu^{II}_{1.5}Na\text{-}A$$
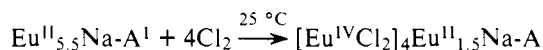
The oxidation is not complete; 1.5 europium ions per unit cell remain in the divalent state. Surprisingly, one Eu(II) ion per unit cell is located on a fourfold axis near the center of an 8-ring, but off its plane. Although this Eu(II) ion does not appear to occupy a single well-defined site, it clearly 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, Na_{12}-A^1, 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,
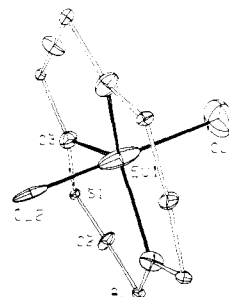

Figure 1. A view of the trigonal-bipyramidal Eu(IV) complex. This structure occurs four times per unit cell. Selected bond lengths in angstroms are Eu(1)-O(3) = 2.31 (1), Eu(1)-Cl(1) = 2.52 (4), and Eu(1)-Cl (2) = 2.06 (3); some bond angles are O(3)-Eu(1)-O(3) = 118.3 (8)°, Cl(1)-Eu(1)-O(3) = 97.5 (8)°, and Cl(2)-Eu(1)-O(3) = 82.5 (8)°. Ellipsoids of 20% probability are shown.
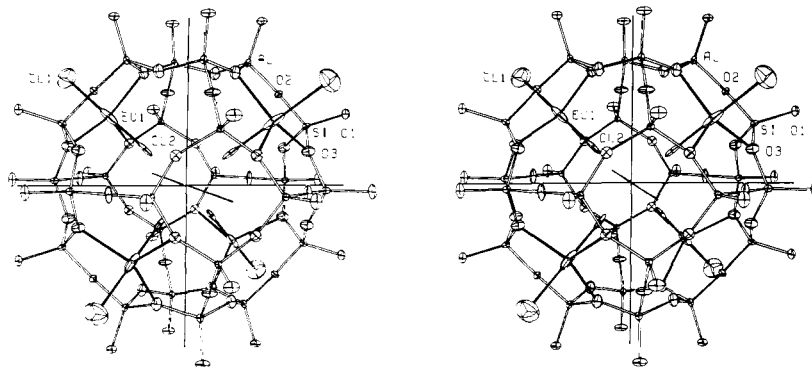
Figure 2. A stereoview of the [Eu^{IV}Cl$_2$]$_4$Eu^{II}$_{1.5}$Na-A sodalite unit. Selected bond lengths in angstroms are (Si,Al)-O(1) = 1.630 (8), (Si,Al)-O(2) = 1.633 (6), and (Si,Al)-O(3) = 1.685 (5). The divalent 6-ring europium ion which occurs in half of the unit cells is not shown. Ellipsoids of 20% probability are shown.

Table I. Positional, Thermal,[a] and Occupancy Parameters for [Eu^{IV}Cl$_2$]$_4$Eu^{II}$_{1.5}$Na-A

	Wyckoff position	x	y	z	β_{11}[b] or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Occupancy factor Varied	Fixed
(Si,Al)	24 (k)	0	1846 (5)	3730 (4)	20 (4)	19 (4)	28 (5)	0	0	13 (8)	1[c]	1[c]
O(1)	12 (h)	0	2242 (17)	½	94 (22)	50 (20)	24 (15)	0	0	0	1	1
O(2)	12 (i)	0	2818 (11)	2818 (11)	108 (24)	23 (9)	23 (9)	0	0	15 (31)	1	1
O(3)	24 (m)	1122 (8)	1122 (8)	3412 (12)	48 (8)	48 (8)	78 (15)	−2 (27)	9 (17)	9 (17)	1	1
Eu(1)	8 (g)	2027 (4)	2027 (4)	2027 (4)	125 (4)	125 (4)	125 (4)	192 (9)	192 (9)	192 (9)	0.54 (1)	0.56
Cl(1)	8 (g)	3214 (18)	3214)18)	3214 (18)	197 (23)	197 (23)	197 (23)	−85 (41)	−85 (41)	−85 (41)	0.46 (5)	½
Cl(2)	8 (g)	1054 (15)	1054 (15)	1054 (15)	75 (12)	75 (12)	75 (12)	126 (31)	126 (31)	126 (31)	0.52 (2)	½
Eu(2)	6 (f)	1032 (71)	½	½	49 (6)						0.17 (3)	⅙

[a] Positional and anisotropic parameters are given × 10⁴. 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_{ii} values using the formula, $\mu_i = 0.225\ a\ (\beta_{ii})^{1/2}$, where a = 12.251 Å. [c] Occupancy for (Si) = ½; occupancy for (Al) = ½.

was sealed in its capillary and removed from the vacuum line by torch.

The space group *Pm3m* (no systematic absences) was used throughout this work for reasons discussed previously.[2a] The structure, a = 12.251 (2) Å at 23 (1) °C, was solved using the 281 unique observed ($I_o > 3\sigma(I_o)$; $2\theta < 70°$) reflections collected by counter methods using a fully automated Syntex P$\overline{1}$ diffractometer with monochromatic Mo Kα radiation (Kα_1, λ = 0.70930 Å; Kα_2, λ = 0.71359 Å) and a pulse-height analyzer. Other experimental details including data reduction are the same as previously presented.[3] The value of x in the formula of the unit cell, Eu$_x$Na$_{12-2x}$Si$_{12}$Al$_{12}$O$_{48}$, exclusive of chloride ions, was determined by refinement of the occupancies of the europium positions; x = 5.5

Least-squares refinement of [Eu^{IV}Cl$_2$]$_4$Eu^{II}$_{1.5}$Na-A began using the atomic parameters of the atoms of the aluminosilicate framework: (Si,Al), O(1), O(2), and O(3).[6] In addition, a probable europium position, Eu(1) (see Table I), was included. A subsequent Fourier difference function clearly revealed the Cl(1), Cl(2), and Eu(2) positions. Full-matrix least-squares refinement[7] using anisotropic temperature factors for all atoms except Eu(2), which was refined isotropically, converged to the error indices, $R_1 = (\Sigma|F_o - |F_c||/\Sigma F_o) = 0.113$ and $R_2 = (\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.089$ with the fixed occupancies shown in Table I. Removing Eu(2) from least-squares increased R_1 and R_2 to 0.123 and 0.120, respectively, at convergence. The varied occupancies shown in Table I resulted from simultaneous positional, occupancy, and thermal parameter refinement of each position; this had little effect on the error indices. The overdetermination ratio is 8.8 for the total of 32 parameters varied in least squares.

Four three-coordinate near-planar europous ions per unit cell have been oxidized by chlorine to the tetravalent state to form five-coordinate near-trigonal-bipyramidal complexes (see Figure 1). This is an oxidative addition reaction. The three-

fold-axis Eu(IV) ions, recessed by 0.3 Å into the large cavity, coordinate equatorially to three 6-ring O(3) oxide ions at 2.31 Å, and axially to two chloride ions at Cl(1) and Cl(2). Cl(1), in the large cavity, is 2.52 Å from Eu(IV), and Cl(2), in the sodalite cavity, makes a much shorter 2.06-Å approach (vide infra).

The occupancy at Eu(1) is 4.5 ions per unit cell. Therefore, by difference, 0.5 europium ion per unit cell at this position must remain divalent since only four ions reacted with chlorine, as is clearly indicated by the occupancy refinement of the chloride positions Cl(1) and Cl(2). (If the occupancy of chloride ions at Cl(2) were greater than four, then unacceptable Cl$^-$-Cl$^-$ approaches of 2.58 Å would result.) This Eu(II) ion, although not equivalent to the four Eu(IV)'s, occupies a position too similar to them to refine separately in least squares.

Finally, one Eu(II) ion per unit cell at Eu(2) occupies a most unusual position on a fourfold axis near an 8-ring. It approaches four O(1) and four O(2) oxide ions of an 8-ring at 3.60 (4) and 3.98 (3) Å, respectively. The closest approach made by the ion at Eu(2) to framework oxide ions is 1.19 Å greater than the sum of the corresponding ionic radii.[8] Based on a distance criterion, this europium ion is considered zero coordinate.[3] Its large isotropic thermal parameter is a logical consequence of (1) the distant approaches it makes to framework oxide ions, and (2) disorder in the direction perpendicular to the 8-ring, as indicated by an electron density difference function which indicated appreciable density at (0.04, ½, ½) as well as (0.10, ½, ½). As a result, anisotropic refinement of Eu(2) failed as its β_{11} thermal parameter became very large.

The association of Eu(II) ions with 8-rings is not new; in the structure of dehydrated Eu^{II}$_{5.75}$-A,[9] one Eu(II) ion per unit cell lies in the plane of an 8-ring exactly at (0, ½, ½), 0.96 Å from the nearest framework oxide ions. It is considered near-

zero-coordinate based on a distance criterion.[9] In $[Eu^{IV}Cl_2]_4$-$Eu^{II}_{1.5}Na$-A, the displacement of the Eu(II) ion at Eu(2) from the plane of its 8-ring may be due to a relatively weak 4.09-Å attraction toward two chloride ions at Cl(1).

It is remarkable that the Eu(II) ion at Eu(2) does not react with chlorine. Perhaps such an ion, unperturbed by a ligand field and nearly unpolarized, is afforded a special stability and is in a sense "unprimed" for attack by chlorine. Perhaps also the coordination number that might result from such attack is inadequately low (i.e., zero-coordinate $Eu^{II} + Cl_2 \rightarrow$ two-coordinate $Eu^{IV}Cl_2$). No additional dichlorine or chloride could be located; in particular, no peaks appeared near the Eu(2) position.

The Eu(1)-Cl(1) and Eu(1)-Cl(2) bond distances are shorter than the sum of the appropriate ionic radii (0.85 Å for Eu(IV)[8,10] and 1.81 for Cl[− 8]), indicating a strong covalent interaction. To date, only relatively weak covalent interactions have been reported for the lanthanides, in a few organolanthanide complexes[11] for example.

Some features of this structure encourage particularly covalent Eu-Cl interactions. First, the zeolite framework itself highly favors the transfer of negative change from the chloride ions to the Eu(IV) ions to lessen the unfavorable concentration of positive charge within the 6-rings. Secondly, because the chloride ions are one coordinate, their charge is transferred more easily to Eu(IV) than it would be if the electrostatic field about the chloride ions were more favorable, that is if the coordination number were greater than one.

There are several unoccupied Eu(IV) orbitals of the correct symmetry to accept electron density from the filled 3p orbitals on chloride. The $4f_{z^3}$, $5d_{z^2}$, or $6p_z$ orbitals could participate in a σ interaction by accepting density from the filled chloride $3p_z$ orbital. In addition, a number of less important π interactions are possible.

The nonequivalence of the two Eu^{IV}-Cl bonds is probably due to the very different environments experienced by the chloride ions. Within the sodalite unit, the four Cl⁻ ions at Cl(2) are arranged tetrahedrally (see Figure 2) such that each Cl⁻ ion is 3.65 Å from the three others. This crowding of anions also acts to facilitate the back-donation of charge to Eu(IV) and contributes to the formation of this uniquely short Eu(1)-Cl(2) bond. In the large cavity, the chloride ions at Cl(1) experience no such crowding. The very unequal thermal ellipsoids at Cl(1) and Cl(2) tend to support this interpretation.

It has been assumed that both chlorine atoms coordinated to Eu(1) are chloride ions. However, the actual electron distribution in the $EuCl_2^{2+}$ complex cannot be established crystallographically. Further work is needed to determine the electronic structure, and therefore the charge, of those europium ions.

The fourth ionization potential of europium is very close to those of other lanthanides whose +4 state is known in the solid (see Table II of ref 4). Accordingly, it is reasonable that Eu(IV) has been prepared and stabilized within zeolite A. It can be anticipated that new high oxidation states of many elements can be similarly stabilized and identified within zeolites.

Supplementary Material Available: Listing of the observed and calculated structure factors (supplementary Table 1, 2 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, $Eu_{5.5}Na$-A represents $Eu_{5.5}NaAl_{12}Si_{12}O_{48}$, exclusive of guest species which may be present within the zeolite, such as water.
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(3) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 1112 (1977).
(4) R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, preceding paper in this issue.
(5) H. Bärnighausen, *Z. Anorg. Allg. Chem.*, **342**, 233 (1966).
(6) These framework parameters were taken from the structure of $[Eu^{IV}-O]_{2.75}Eu^{II}_{1.75}Na_3$-A. See ref 4.
(7) Principal computer programs used in this study: T. Otterson, 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.
(8) "Handbook of Chemistry and Physics", 55th ed, The Chemical Rubber Co., Cleveland, Ohio, 1974, p F190.
(9) The complete unit cell formula is $Eu_{6-x}Na_{2x}Al_{12}Si_{12}O_{48}$, $0 \le x \le 0.5$: R. L. Firor and K. Seff, *J. Am. Chem. Soc.*, **99**, 7059 (1977).
(10) This radius was obtained by extrapolation and by comparison with Ce(III) and Ce(IV).
(11) N. M. Ely and M. Tsutsui, *Inorg. Chem.*, **14**, 2680 (1975).

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Cyclopropa[3,4]benzocyclobutene[1]

Sir:

We report the synthesis of cyclopropa[3,4]benzocyclobutene (**1**), the second isomer of benzene annelated with a three- and a four-membered ring, the other isomer, cyclopropa[4,5]benzocyclobutene (**2**) having recently been reported by ourselves[2] and others.[3]

Our initial attempts to prepare **1** were modeled on our synthesis of **2**; 7,7-dichloro-2,3-bis(methylene)bicyclo[4.1.0]-heptane (**3a**),[4,5] prepared in a similar manner to the corresponding 3,4-bis(methylene) compound,[2] was irradiated with a Hanovia 250-W lamp through quartz to give the cyclobutene **4** in 50% yield.[4,5] Treatment of **4** with KO-*t*-Bu under a variety of conditions gave none of the desired **1**. The 7,7-dibromodiene **3b**[4,5] was also prepared, but photochemical ring closure could not be effected.[6] The failure of **4** to give **1** might have been due to the position of the double bond, since we have also been unable to synthesize cyclopropa[*a*]naphthalene or biscyclopropa[*a,e*]naphthalene by this route,[7] and no examples of the Billups' reaction[9] were known in which the double bond is in the 2,3 rather than the 3,4 position. Accordingly, we prepared **5** and subjected it to reaction with KO-*t*-Bu, when it was