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$_2$ → 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.
(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.*, **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 ≤ x ≤ 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).
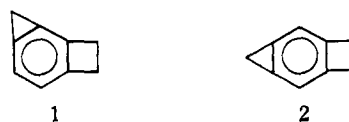
**R. L. Firor, K. Seff***
*Chemistry Department, University of Hawaii*
*Honolulu, Hawaii 96822*

### 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]



1                    2

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
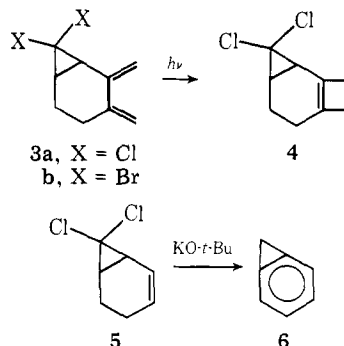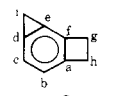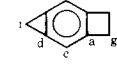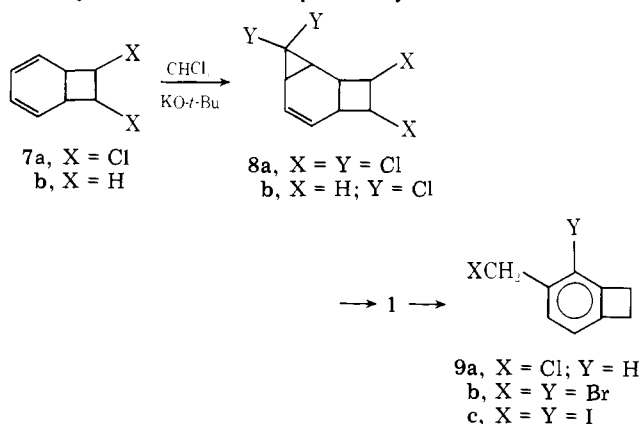


3a, X = Cl          4
b, X = Br



5                    6

Table I. ^{13}C NMR Shifts and [1]$J_H$ Coupling Constants in 1 and 2

| | | | Carbon chemical shifts, ppm,[a] and coupling constants (Hz) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | a | b | c | d | e | f | g | h | i | Ref |
|  | 148.0 | 121.0 (162) | 112.4 (166) | 126.0 | 119.6 | 135.9 | 31.1 (138) | 30.9 | 19.9 (170) | b |
|  | 145.5 | | 110.0 (169) | 122.8 | | | 29.0 (137) | | 19.2 (169.5) | c |

[a] Peaks measured from CDCl$_3$ which was taken as 77.2 ppm downfield from Me$_4$Si. [b] These assignments are based on relative peak heights, proton–carbon coupling, and comparison of the shifts with those in benzocyclopropene and benzocyclobutene. [c] These values are from ref 2.

smoothly converted into benzocyclopropene (6). The rate of conversion of 5 into 6 did, however, appear slower than the rate of conversion of the 3,4 isomer into 6, and the fact that the double bond in 4 is tetrasubstituted might be critical, particularly if prior rearrangement to the 3,4 position has to occur.[10] Consequently the preparation of an isomer of 4 with the double bond in a different position was investigated.

The diene 7a, prepared by the chlorination of cyclooctate-traene,[11] was treated with KO-$t$-Bu and CHCl$_3$ to give the dichlorocarbene adduct 8a, mp 78–79 °C, in 28% yield.[4,5] All attempts to replace the cyclobutyl chlorine atoms with hydrogen were unsuccessful. Bicyclo[4.2.0]octa-2,4-diene (7b) was therefore prepared,[12] which on treatment with KO-$t$-Bu and CHCl$_3$ gave the adduct 8b in 35% yield.[4,5] Treatment of 8b (1.0 g, 5.3 mmol) with KO-$t$-Bu (2.24 g, 20 mmol) in Me$_2$SO (20 mL) at 15 °C for 5 min gave 1 (25 mg, 0.2 mmol, 4%).[13] The mass spectrum (20 eV) had $m/e$ (rel intensity) 116 (M$^+$, 45%), 115 (M$^+$ − 1, 100%); high resolution (70 eV) 116.0632 (C$_9$H$_8$ requires 116.0625). The ^{1}H NMR spectrum (CCl$_4$) showed an AB quartet at $\delta$ 7.04 and 6.82 (2 H, $J$ = 6.5 Hz), a singlet at 3.24 (4 H), and a singlet at 3.18 (2 H),[14] and the ^{13}C NMR spectrum had nine absorptions (Table 1). The electronic spectrum (hexane) showed a broad band with maxima at 264 nm (sh, log $\epsilon$ ~3.1) 270 (~3.2), and 276.5 (~3.2).[15] These data are clearly in accord with the assigned structure. Comparison of the ^{13}C NMR spectra of 1 and 2 is made in Table 1, and the chemical shifts found for 1 could be directly derived from those previously found for 2.



7a, X = Cl
 b, X = H

8a, X = Y = Cl
 b, X = H; Y = Cl



→ 1 →

9a, X = Cl; Y = H
 b, X = Y = Br
 c, X = Y = I

The electronic spectrum shows the expected hypsochromic shift compared with that of 2, but the deviation from the trend observed by Thummel and Nutakul[16] for benzenes annelated in the 1,2:3,4 positions by larger rings is less than that for 2 with its related systems.[17]

Treatment of 1 with HCl in CCl$_4$ gave 9a,[4,5] identical with the compound obtained by a similar treatment of 2, and therefore having the constitution shown. Treatment of 1 with Br$_2$ gave 9b, mp 77–78 °C,[4,5] and with I$_2$ gave 9c, mp 79–81 °C,[4,5] the substitution pattern being assumed on the basis of the structure of 9a.[18,19]

We are currently engaged in a comparative study of the chemistry of 1 and 2.

**References and Notes**

(1) Tricyclo[6.1.0.0$^{2,5}$]nona-1,5,7-triene.
(2) D. Davalian and P. J. Garratt, *J. Am. Chem. Soc.*, **97**, 6883 (1975).
(3) C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 4539 (1975).
(4) Satisfactory microanalytical and/or high resolution mass spectral data have been obtained for this compound.
(5) ^{1}H NMR ($\delta$): 3a (CDCl$_3$), 5.53 (s, 1 H), 5.12 (s, 2 H), 4.70 (s, 1 H), 2.10 (m, 6 H); 3b (CDCl$_3$), 5.66 (s, 1 H), 5.23 (s, 2 H), 4.76 (s, 1 H), 2.13 (m, 6 H); 4 (CDCl$_3$), 2.62 (m, 2 H), 2.45 (m, 2 H), 1.94 (m, 6 H); 8a (CDCl$_3$), 6.12 (ddd, 1 H, $J$ = 9, 6, 1 Hz), 5.84 (dd, 1 H, $J$ = 10, 2 Hz), 4.30 (m, 2 H), 3.38 (t, 1 H, $J$ = 10 Hz), 2.86 (m, 1 H), 2.18 (m, 2 H); 8b (CDCl$_3$), 6.0 (m, 2 H), 3.2–1.2 (m, 8 H); 9a (CCl$_4$), 6.96 (m, 3 H), 4.40 (s, 2 H), 3.06 (s, 4 H); 9b (CCl$_4$), 7.24, 6.90 (dd, 2 H, $J$ = 7.5 Hz), 4.52 (s, 2 H), 3.12 (s, 4 H); 9c (CCl$_4$), 7.24, 6.88 (dd, 2 H, $J$ = 7.5 Hz), 4.50 (s, 2 H), 3.02 (s, 4 H).
(6) Decomposition occurred under the reaction conditions.
(7) The properties of cyclopropa[a]naphthalene, which has now been prepared,[8] suggest that even if formed this compound would not have survived our isolation procedure.
(8) S. Tanimoto, R. Schafer, J. Ippen, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **15**, 613 (1976).
(9) W. E. Billups, A. J. Blakeney, and W. Y. Chow, *J. Chem. Soc. D*, 1461 (1971).
(10) Also, unlike the case of the 3,4 isomer, elimination of HCl from 5 can proceed in two ways, and one of the dienes so produced requires more extensive bond rearrangement to give 6.
(11) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952).
(12) K. Alder and H. A. Dortmann, *Chem. Ber.*, **87**, 1492 (1954).
(13) The method of isolation was similar to that described by Billups et al.[9] Compound 1 has a pungent smell, similar to benzocyclopropene, and the yield without distillation is ~10% (NMR).
(14) At 60 MHz with CDCl$_3$ as solvent, a single resonance is observed for the cyclopropyl and cyclobutyl hydrogens.
(15) These are minimal values for the extinction coefficients.
(16) R. P. Thummel and W. Nutakul, *J. Org. Chem.*, **42**, 300 (1977).
(17) It is not at present possible to compare the degree or direction of bond fixation in these two systems. The ^{13}C NMR spectra indicate that both systems are similarly hybridized at comparable carbon atoms, but the significance of the large bathochromic shift in the electronic spectrum of 2 is not known.
(18) The ^{1}H NMR spectrum of 9c shows two low intensity singlets at 4.32 and 3.12 (1:2), probably due to the other isomer.
(19) Chemical proof for the substitution pattern in 9b and 9c is currently being sought.

**Dariush Davalian, Peter J. Garratt***
**Muzammil M. Mansuri**
*Department of Chemistry, University College London*
*London WC1H OAJ, England*
*Received August 24, 1977*

## On the Nature of Ru(bpy)$_3$$^+$ in Aqueous Solution[1]

*Sir:*

Ru(bpy)$_3$$^+$ (bpy = 2,2'-bipyridine) is generated[2-5] upon the reductive quenching of *Ru(bpy)$_3$$^{2+}$ and is thermodynamically capable of reducing H$_2$O to H$_2$.[6,7] Thus, Ru(bpy)$_3$$^+$ could be