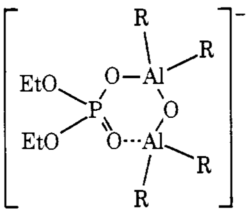
a "chelate" anionic complex with the phosphate residue, e.g., **10**.[11] Of these reagents, tetraisobutyldialuminoxane (**11**)



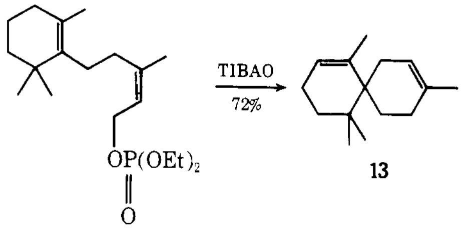
10

$(i\text{-Bu})_2\text{Al—O—Al}(i\text{-Bu})_2$

11

prepared by the action of 0.5 equiv of water on diisobutylaluminumhydride in dry THF (at −78° under argon)[12] followed by concentration in vacuo was clearly the most effective; the reagent is designated herein as TIBAO. The reaction of the ester **3** with 4.0 mol equiv of TIBAO in methylene chloride at 0° for 1 h and 20° for 3 h produced limonene (66%) and terpinolene (9%) exclusively: none of the other by-products were detected by GLC and TLC analyses. TIBAO-promoted cyclization did not suffer the significant solvent effects and the use of hexane or THF as solvent afforded **4** and **5** in yields of 54 (**4**:**5** = 9:1) and 80% (5:3), respectively. Surprisingly, the geranyl ester **1** also experienced the similar cyclization with equal efficiency (75% yield; 5:3) by exposure to excess TIBAO in THF, probably due to the intermediacy of "free" allylic carbonium ion in this reagent-solvent system.[13]

To illustrate the utility of the "aluminum promoted" cyclization process in an even more complex case, the cyclization of (*Z*)-monocyclofarnesyl diethyl phosphate (**12**)[14] was chosen to study. Previously (*Z*)-monocyclofarnesol was transformed into α-chamigrene (**13**) in low relative yield.[15,16] After examining several organoaluminum reagents in various solvent systems, we soon found that TIBAO was the reagent of choice for the substrate **12**.[17] Thus, the cyclization was carried out with excess TIBAO (10 equiv) in hexane at −78° for 10 h and 20° for 3 h to produce *dl*-α-chamigrene (**13**)[18] in 72% yield accompanied by only ~3% of the β-isomer.



12 **13**

The investigation is currently being extended to ascertain in more detail the scope of these reactions which may have theoretical and synthetic value. We are particularly intrigued with possibilities to control the cyclization process regio- and stereoselectively.

References and Notes

(1) For a review dealing with terpene terminal epoxide cyclization, see E. E. van Tamelen, *Acc. Chem. Res.*, **1**, 111 (1968). For a related biogenetic-like cyclizations, see W. S. Johnson, *ibid.*, **1**, 1 (1968); K. E. Harding, *Bioorg. Chem.*, **2**, 248 (1973).

(2) Haley, Miller, and Wood have examined the behavior of geranyl and neryl phosphate, as model for the biosynthetic process. These compounds decompose slowly at 37° in inert solvents to give a complex mixture of acyclic and cyclic hydrocarbons: R. C. Haley, J. A. Miller, and H. C. S. Wood, *J. Chem. Soc. C*, 264 (1969). See also W. Rittersdorf and F. Cramer, *Tetrahedron*, **24**, 43 (1968), **23**, 3015, 3023 (1967); P. Valenzuela and O. Cori, *Tetrahedron Lett.*, 3089 (1967).

(3) General review: J. H. Richards and J. B. Hendrickson, "The Biosynthesis of Steroids, Terpenes, and Acetogenins", W. A. Benjamin, New York, N.Y., 1964. A reasonable biosynthetic route for presqualene pyrophosphate, which involves the formation of a C-S bond from an allyl pyrophosphate, was reported: T. Cohen, G. Herman, T. M. Chapman, and D. Kuhn, *J. Am. Chem. Soc.*, **96**, 5627 (1974).

(4) Prepared in 80-90% yields from diethyl chlorophosphate and geraniol: A solution of geraniol (or nerol) in ether at −78° was treated with *n*-butyllithium (1 equiv) using *o*-phenanthroline as the internal indicator, followed by diethyl chlorophosphate (2 equiv) in ether-triethylamine (treatment of the chloride with triethylamine at 0° in ether produced the white precipitate and the clear supernatant was used) at −20° for 20 h. Chromatography on silica gel column (hexane-ethyl acetate) furnished the pure ester, homogeneous by TLC analysis and spectroscopically consistent with the indicated structure.

(5) An *E,Z* mixture of the diene **2** was prepared independently from 6-methyl-5-hepten-2-one and propylidenetriphenylphosphorane in THF. Reaction of **1** or **3** with MeMgI in ether produced a low yield of **2** (*E-Z* mixture), see also ref 2.

(6) The formation of cyclic hydrocarbons from geranyl diphenyl phosphate under solvolysis conditions was reported by Miller (ref 2). It is suggested that participation by the P═O bond occurs and that geranyl phosphate rearranges to linalyl phosphate which cyclizes with ease, although they were unable to identify linalyl phosphate in the reaction mixture.

(7) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(8) J. I. Jones and W. S. McDonald, *Proc. Chem. Soc., London*, 366 (1962).

(9) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **21**, 2683 (1968).

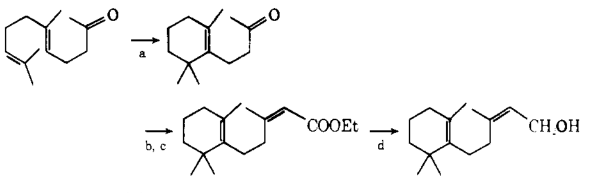
(10) Bis(diethylaluminum) sulfide: H. Imaeda, T. Hirabayashi, K. Itoh, and Y. Ishii, *Organomet. Chem. Synth.*, **1**, 115 (1970/1971). Bis(dimethylaluminum) anilide: H. Tani and N. Oguni, *J. Polym. Sci. B*, **3**, 123 (1965). Tetraisobutyldialuminoxanes: T. R. Crompton, *Anal. Chem.*, **39**, 1464 (1967).

(11) The requirement for a divalent metal ion is found in most enzymic reactions of phosphate ester heterolysis, see T. C. Bruice and S. Benkovic, "Bioorganic Mechanisms", Vol 2, W. A. Benjamin, New York, N.Y., 1966, p 167. TIBAO might play a similar important role for the present reaction.

(12) G. B. Sakharovskaya, N. N. Korneev, A. F. Popov, Y. V. Kissin, S. M. Mezhikovskii, and E. Kristalnyi, *J. Gen. Chem. USSR (Engl. Transl.)*, **39**, 749 (1969).

(13) The ether solvent–TIBAO combination might increase the lifetime of geranyl carbonium ion so that it can be converted into neryl carbonium ion which cyclizes with ease. For similar solvent effects, see C. A. Bunton, J. P. Leresche, and D. Hachey, *Tetrahedron Lett.*, 2431 (1972).

(14) The phosphate **12** was prepared by esterification (ref 4) of (*Z*)-monocyclofarnesol, in turn made readily available by a synthesis developed in this laboratory:



where (a) HCOOH; (b) $Me_3SiCHLiCOOEt$; (c) *E,Z* separation by chromatography on silica gel; (d) AlH_3.

(15) S. Kanno, T. Kato, and Y. Kitahara, *Chem. Commun.*, 1257 (1967).

(16) The acid-catalyzed isomerization of (−)-thujopsene under nonaqueous conditions was known to proceed via α- and β-chamigrene to a complex mixture of isomeric tricyclic hydrocarbons: H. U. Daeniker, A. R. Hochstetler, K. Kaiser, and C. C. Kitchens, *J. Org. Chem.*, **37**, 1 (1972); W. G. Dauben and L. E. Friedrich, *ibid.*, **37**, 241 (1972); W. G. Dauben and E. I. Aoyagi, *ibid.*, **37**, 251 (1972).

(17) Other aluminum reagents or TIBAO in other solvent systems gave relatively low yields of desired products.

(18) Identical in all respects with the authentic sample. We thank Professor S. Torii and associates for a generous comparison sample and spectral data of α-chamigrene; J. D. White, S. Torii, and J. Nogami, *Tetrahedron Lett.*, 2879 (1974).

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Zero-Coordinate Rb$^+$. A Rubidium Ion Whose Interionic Contacts Are All Unconventionally Long by More Than 1.5 Å

Sir:

Large monovalent cations were observed to be under-coordinated in the crystal structures of the dehydrated zeolites Cs_7Na_5-A[1,2] and K_{12}-A.[2,3] In the latter structure, a zero-coordinate K^+ ion is located deep within the zeolite's large cavity, 4.25 Å from the nearest framework ion, an oxygen.[4] This distance is 1.6 Å greater than the sum of the corresponding ionic radii.[5]

Herein is reported a substantiation of that result, the existence of an uncoordinated Rb^+ ion in Rb^+-exchanged zeolite A. This work is more precise than that involving K_{12}-A because

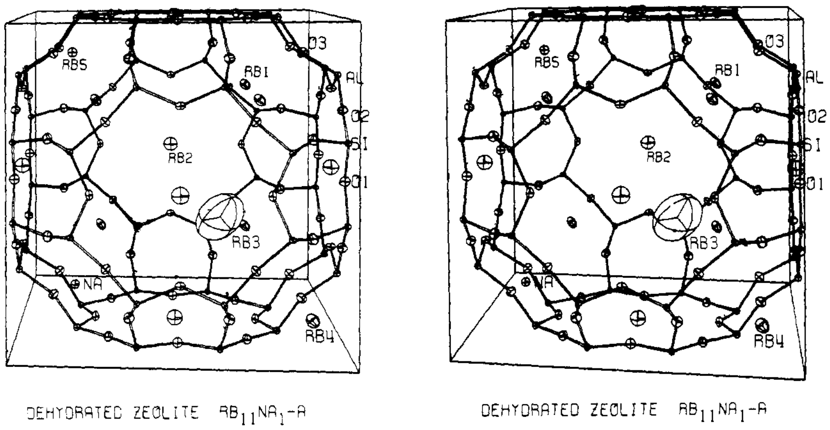

Figure 1. A stereoview of the $Rb_{11}Na_1$-A unit cell is shown. Ellipsoids of 20% probability are used. Selected bond lengths (in Å) are (Si, Al)-O(1) = 1.673 (5), (Si,Al)-O(2) = 1.652 (3), (Si,Al)-O(3) = 1.664 (2), Na-O(3) = 2.411 (7), Rb(1)-O(3) = 2.716 (7), Rb(2)-O(1) = 3.181 (10). Rb(4)-O(3) = 2.949 (17), Rb(5)-O(3) = 2.608 (12); some bond angles are O(3)-Rb(1)-O(3) = 100.5 (3)°, O(3)-Rb(4)-O(3) = 90.5 (5)°, O(3)-Rb(5)-O(3) = 106.4 (3)°, and O(3)-Na-O(3) = 119.9 (6)°.

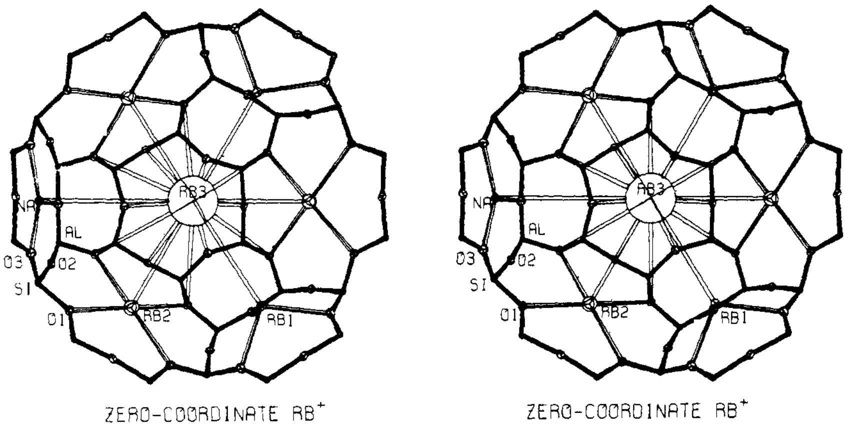

Figure 2. A stereoview, approximately along the threefold axis, of half of the large cage, showing all Rb(3)-O distances less than 5.0 Å and all Rb(3)-Rb distances less than 5.3 Å. Rb(3) is 4.35(8) Å from three O(3)'s, 4.64(8) Å from three O(2)'s, 4.99(5) Å from six O(1)'s, 5.04(1) Å from three Rb(2)'s, 5.11(2) Å from two Rb(1)'s, and 6.24(1) Å from Na. A Rb(4) ion 5.31 (10) Å from Rb(3) along the direction of view is not shown.

(1) the x-ray scattering factor is about twice as big for Rb^+ as for K^+, and (2) almost twice as many diffraction data were gathered from a crystal 50% larger by volume. The structure is nearly the same as that of K_{12}-A.[3]

A single crystal of sodium zeolite 4A, 0.10 mm on an edge, was lodged in a fine glass capillary. RbOH (0.1 M) was allowed to flow past the crystal at about 1.0 cm/s for 8 days. The crystal was dehydrated for 48 h at 350 °C and 1×10^{-5} Torr. Its appearance was unaltered by these exchange and dehydration procedures.

The structure was studied in the cubic space group $Pm3m$[4a] (a = 12.261 (2) Å at 23 (1) °C) by counter methods. It was solved using 300 unique observed ($I_o > 3\sigma(I_o)$: $3° < 2\theta < 70°$) reflections. An absorption correction was applied but it had no significant effect. Occupancy refinement indicated a cation composition of $Rb_{11}Na_1$ per unit cell; this zeolite will subsequently be referred to as $Rb_{11}Na_1$-A. The concurrently completed structure of hydrated $Rb_{11}Na_1$-A verifies this cationic composition.

Least-squares refinement[6] of $Rb_{11}Na_1$-A began using the principal cation coordinates (adjusted to account for differing ionic radii) and framework positions of K_{12}-A[3]. A subsequent Fourier function had a peak about 3.9 $eÅ^{-3}$ in height at (0.36, 0.36, 0.36). This position, indicative of an uncoordinated Rb^+ ion, Rb(3), was stable in least-squares refinement. The occupancies of Rb(1) and Rb(2) refined unambiguously to five and three ions per unit cell, respectively. Anisotropic refinement of the framework and Rb^+ positions, Rb(1) through Rb(4), and isotropic refinement of Rb(5) and Na^+, quickly converged to an R_2 weighted index, $(\Sigma w(F_o - |F_c|)^2/\Sigma wF_0{}^2)^{1/2}$, of 0.055. A trial removal of Rb(3) from least-squares refinement increased R_2 to 0,063, An unsuccessful attempt was made to refine an alternative structure based on ten Rb^+ ions (Rb(3) absent) and two Na^+ ions.

The crystal studied was dehydrated; the unusual Rb(3) position cannot be attributed to residual water molecules. The dehydration conditions employed were more than sufficient to remove all water from Na^+, K^+, Co(II), and Mn(II),[7] and Rb^+ is more labile toward water exchange than any of those. If Rb(3) were occupied by a water oxygen instead of Rb^+, the hydration distance to Rb(1) would be 2.37 Å, far from the acceptable 2.88 Å distance observed in the subsequently determined structure of hydrated $Rb_{11}Na_1$-A. The 11 Rb^+ ions located in that structure must remain present after dehydration, and one Rb^+ cannot be placed elsewhere than at Rb(3).

In the structure of dehydrated $Rb_{11}Na_1$-A (see Figure 1), 8 of the 11 Rb^+ ions per unit cell are distributed over four nonequivalent threefold-axis equipoints, while the remaining three, at Rb(2), lie at the centers of the 8-oxygen rings. The Rb(1) ions, of which there are five, are located in the large cavity, 1.25 Å from the O(3) planes of the oxygen 6-rings. Two nonequivalent Rb^+ ions, Rb(4) and Rb(5), are located inside the sodalite unit near the 6-rings, 1.69 and 0.99 Å, respectively, from the [111] plane at O(3). Rb(3), the uncoordinated ion, is located deep within the large cavity, 3,62 Å from the O(3) plane (Figure 2). Its closest approach to a framework oxygen (three O(3)'s of a 6-ring) is 4.35(8) Å, which is 1.56 Å greater than the sum of corresponding ionic radii.[5] The large thermal ellipsoid of this Rb^+ ion is very similar in magnitude and orientation to that of its corresponding K^+ ion in K_{12}-A,[3] and is consistent with its environment. The position of Rb(3) cannot be governed by electrostatics alone; Laplace's equation, $\nabla^2 V = 0$, implies that no purely electrostatic minimum for Rb(3) can exist in any intrazeolitic void. Apparently, the usual chemical attractive and repulsive forces have balanced to give a shallow energy minimum at an unusual position.

The three Rb(2) ions are located at the centers of the 8-oxygen rings, filling that equipoint, at sites of D_{4d} symmetry. The shortest Rb(2)-O distance is long by 0.4 Å,[5] indicating that these ions are "loosely bound". This was observed spectroscopically[8] in hydrated partially Rb^+-exchanged zeolite A, and crystallographically in both hydrated and dehydrated Cs_7Na_5-A.[1]

For zero-coordinate cations to occur, the zeolite must have a high Al/Si ratio, which leads to a high anionic charge density. This ratio is 1.0 in zeolite A, its maximum value according to Loewenstein's rule.[9] Secondly, large monovalent cations are required which "coat" the inner surface of the zeolite, filling all possible coordination sites before all negative charges of the framework have been balanced. In dehydrated K_{12}-A[3] and $Rb_{11}Na_1$-A, only 11 cations per unit cell can locate at sites in conventional contact with the zeolite framework. The twelfth negative charge is balanced by a cation for which no framework coordination site remains available, as in the children's game, "musical chairs".

These results allow us to employ a stringent definition of noncoordination. If the distance between two ions exceeds the sum of their corresponding radii by more than 1.0 Å, then these ions may be considered not bonded or uncoordinated. At least, their bond order is much less than one. On this basis, Rb(3) is termed zero-coordinate, zero being the sum of integers, all zero, describing its bond orders to its nearest neighbors. For this particular structure, the rounded-off value of 1.0 Å used in the criterion stated above may be raised to 1.5 Å.

References and Notes

(1) T. B. Vance, Jr., and K. Seff, *J. Phys. Chem.*, **79**, 2163 (1975).

(2) The nomenclature refers to the contents of the unit cell. For example, Cs_7Na_5-A represents $Cs_7Na_5Al_{12}Si_{12}O_{48}$, exclusive of water molecules if a hydrated crystal is considered.

(3) P. C. W. Leung, K. B. Kunz, I. E. Maxwell, and K. Seff, *J. Phys. Chem.*, **79**, 2157 (1975).

(4) 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).

(5) "Handbook of Chemistry and Physics", 54th ed, The Chemical Rubber Company, Cleveland, Ohio, 1973.

(6) Principal programs used in this study were: LP-73 data reduction program, T. Ottersen, University of Hawaii, 1973; Full-matrix Least-squares, P. K. Gantzel, R. A. Sparks, and K. N. Trueblood, UCLALS4, American Crystallographic Association Program Library (old) No. 317 (modified); Fourier, C. R. Hubbard, C. O. Quicksall, and R. A. Jacobson, Ames Laboratory Fast Fourier, Iowa State University, 1971, modified; C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(7) K. Seff, *Acc. Chem. Res.*, **9**, 121 (1976).

(8) I. E. Maxwell and A. Baks, *Adv. Chem. Ser.*, **No. 121**, 87 (1973).

(9) Loewenstein, W., *Am. Mineral.*, **39**, 92 (1954).

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Resonance Raman Spectroscopy with Unsymmetrically Isotopic Ligands. Differentiation of Possible Structures of Hemerythrin Complexes

Sir:

Resonance Raman spectroscopy has been used successfully to probe chromophoric functional centers in several metalloproteins. With the nonheme oxygen-carrier hemerythrin, the vibrational frequencies revealed by resonance Raman lead to an assignment of a peroxide-type, O_2^{2-}, electronic state for the bound dioxygen.[1,2] It also has been apparent to us that unsymmetrically labeled isotopic ligands (e.g., $^{16}O^{18}O$, and $^{15}N^{14}N^{14}N^-$) might be employed to discriminate among alternative geometric arrangements of ligands at the functional site.

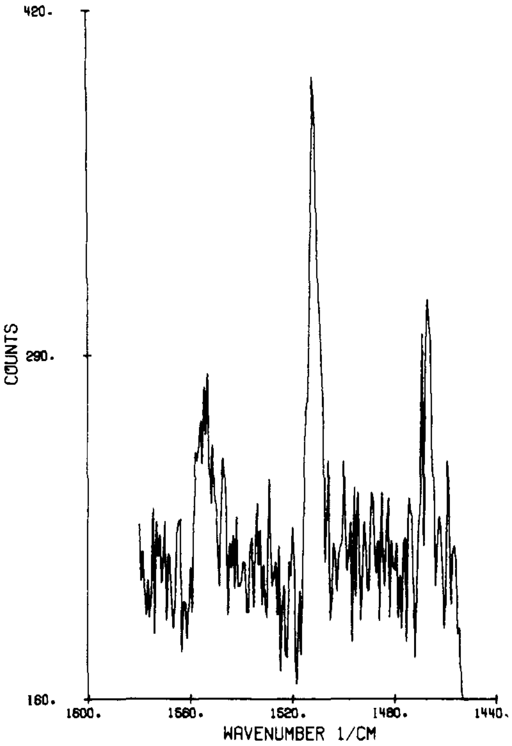
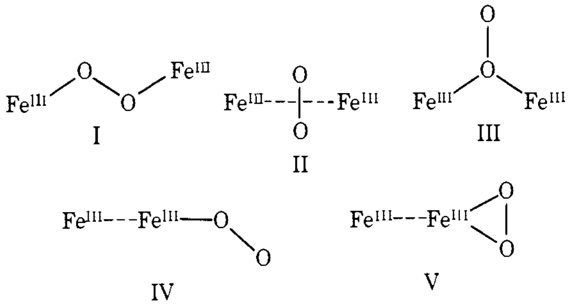


Figure 1. Raman spectrum in the ν_{O-O} region of 58 atom % ^{18}O oxygen gas. Spectrum obtained through a sealed glass ampoule with 90° scattering geometry; laser excitation, 514.5 nm, 150 mW; 3 cm^{-1} spectral slit.

With dioxygen as ligand, the following structural representations have been suggested:[3-8]



With $^{16}O^{18}O$, single symmetric O-O and Fe-O stretching frequencies, ν_{OO} and ν_{Fe-O}, respectively, would be expected for structures I, II, and V, whereas ν_{OO} and ν_{Fe-O} should each be doublets if dioxygen is bound as shown in III or IV because of the two possible modes of attachment of the unsymmetrical ligand. In view of the difficulty in obtaining a sample of pure $^{16}O^{18}O$, the experiments were performed with a mixture of the isotopic species $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (58 atom % ^{18}O from Miles Laboratories). A Raman spectrum of the gaseous dioxygen sample (Figure 1) reveals relative peak heights and relative peak areas of 1:2.6:1.4 each, for the O-O stretch of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$, respectively. The ν_{O-O} region of the resonance Raman spectrum of oxyhemerythrin prepared with this isotopic mixture of dioxygen gas should resemble Figure 1 if structure I, II, or V is a correct representation. Instead we see in the resonance Raman spectrum of oxyhemerythrin (4 mM in 0.1 M Tris-cacodylate, pH 8) prepared with this same dioxygen sample (Figure 2) three bands in the O_2 stretching region with relative areas of 1:2.7:1.5 but with the central peak