In conclusion, a new radical rearrangement, initiated by radical cyclization between ketones and acetylenes followed by β-cleavage of the alkoxy radical and subsequent radical-olefin cyclization, was developed. This reaction realized a single-step conversion from cyclohexanone derivatives to bicyclic cycloheptanones and cyclooctenones. Since the substrates were readily obtainable by using standard methods and the operation is very simple, this reaction allows an easy access to such skeletons. Further investigations to determine the scope and limitations of this reaction and applications to the natural product synthesis are now underway.

Acknowledgment. We thank Professor A. G. M. Barret, Northwestern University, for discussion about the mechanism of this reaction.

Supplementary Material Available: Experimental procedures for preparing **4a** and **7b** as well as full characterization data for **4a**, **5**, **7b**, **8**, and **9** (2 pages). Ordering information is given on any current masthead page.

From the Molecule to an Expanded I-VII Semiconductor Quantum Superlattice: Silver,Sodium Halo-Sodalites

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Silver bromide exhibiting molecular behavior was produced inside an aluminosilicate matrix by substoichiometric silver ion exchange of sodium bromo-sodalite. At increased Ag^+ concentrations up to complete silver exchange, the product is better described as a sodalite lattice containing "expanded silver bromide". Sodalite is unique as a host material, as it consists of bcc packed β-cages that allow trapping of in situ generated molecules and clusters and, therefore, chemical fabrication of monodispersed quantum ultramicrostructures.[1]

Highly crystalline Na,X-sodalites (X = Cl, Br, I) were synthesized hydrothermally as powders or single crystals (1-2 mm).[2] XRD powder patterns showed that the product crystallinity was maintained after the $AgNO_3/NaNO_3$ melt exchange at 320 °C. Results obtained from far- and mid-IR spectroscopy and powder XRD indicate that in mixed sodium,silver halo-sodalites the cations are distributed statistically (a solid solution of $(Na^+)_n(Ag^+)_{4-n}X$ clusters, n = 0-4).

Rietveld refinements of high-resolution X-ray powder data[3] showed that in fully Ag-exchanged halo-sodalites the Ag-X distances are ca. 8% shorter (2.537 (2) Å, 2.671 (2) Å, 2.779 (2) Å for X = Cl, Br, I, respectively) than in the rock-salt bulk materials. The intracage Ag-Ag separations are ca. 6% longer than in the salts (4.142 (2) Å, 4.361 (2) Å, 4.539 (2) Å for X = Cl, Br, I, respectively) and Ag-Ag distances between cages from 25% to 12% longer (4.920 (2) Å, 4.859 (2) Å, 4.821 (2) Å, respectively). Thus one can consider the Ag_4X units as expanded silver halide semiconductors, although electronic band calculations must take into account the effect of the aluminosilicate host matrix.

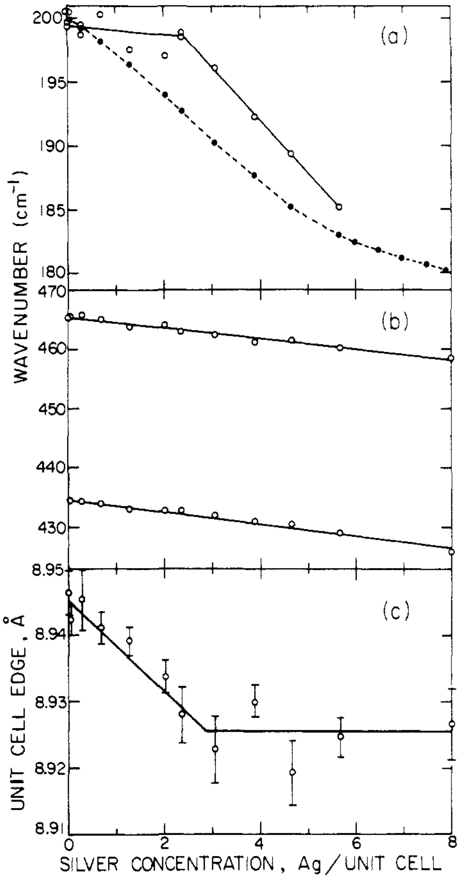

Figure 1. Effect of silver loading on structural and spectroscopic properties of Na,Ag,Br-sodalites. (a) Variations in far-IR Na^+ translatory frequencies with Ag^+ loading (—, untreated samples; - - -, simulated peak positions assuming a binomial distribution of $Na_nAg_{4-n}Br$ moieties with absorption frequencies centered around equally spaced positions between the n = 0-4 extrema). (b) Variations in the mid-IR framework vibrations. (c) Variations in the unit-cell edge.

The Rietveld refinement of Na,Ag,Br-sodalite containing 0.3 Ag^+/unit cell (uc) yielded an Ag-Br bond length of 2.21 Å. A relatively large isothermal temperature factor for the bromide ion of $\langle U \rangle^2$ = 0.052 Å^2 indicates that the anion may be slightly displaced from the center of the cage. After correction for the thermal ion motion,[4] the mean separation of Ag and Br falls in the range 2.21-2.24 Å. A more extreme view based on three standard deviations yields a range from 2.0 to 2.4 Å. This distance compares with the internuclear separation of gaseous Ag-Br (2.39 Å).[5] The Na-Br distance in this sodalite is 2.94 Å, i.e., only 2% shorter than in the salt. Due to the more extensive covalent bonding of AgBr compared to NaBr, the Na_3AgBr aggregate behaves like a slightly perturbed AgBr molecule. On the basis of a binomial distribution of $Na_nAg_{4-n}Br$ moieties, at the silver loading level of this sample one in every eight cages is occupied with an AgBr molecule. The connectivity of AgBr molecules between cages is therefore small, and the AgBr molecules can be considered isolated.

Figure 1 shows that the mid-IR frequency of the aluminosilicate framework vibrations varies linearly with the silver concentration. However, both the far-IR absorptions associated with a translatory mode of Na^+ near the sodalite six-ring site,[6] and the cell edge of the cubic sodalite cage, exhibit abrupt breaks at loading levels near 2.5-3 Ag^+/uc. Both effects may be related to a percolation threshold for connectivity between AgBr units. The unit-cell size decreases slightly as the silver concentration is increased, forming a tighter, more covalent bond between the guest cation and the

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Molecular Absorptions/Absorption Edges (eV)

	AgCl	AgBr	AgI	Order
Molecule	5.12,5.85	4.00,5.04	3.56,4.72	Cl > Br > I
Expanded SC	3.83	3.85	3.76	Cl ≤ Br > I
Bulk SC	3.25	2.68	2.33	Cl > Br > I
SOD Unit Cell Size (Å)	8.8708	8.9109	8.9523	Cl < Br < I

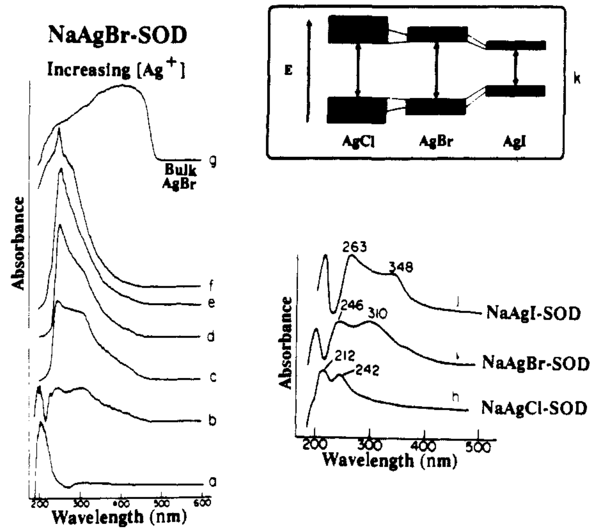

Figure 2. UV–visible reflectance spectra of Na,Ag,Br–sodalites with varying silver concentrations. Ag^+/uc: (a) 0; (b) 0.05; (c) 0.28; (d) 2.0; (e) 3.1; (f) 8.0; (g) bulk AgBr; (h) Na,Ag,Cl–sodalite, 0.1 Ag^+/uc; (i) Na,Ag,Br–sodalite, 0.1 Ag^+/uc; (j) Na,Ag,I–sodalite, 0.1 Ag^+/uc. Note that band-gap absorptions for Na,X-SOD expanded insulators peak at 192 (Cl), 208 (Br), and 214 nm (I) (Figure 2h, i, j) and parallel the order for the bulk fcc NaX materials, 138 (Cl), 165 (Br), and 211 nm (I), respectively.[12] (k) Schematic band diagram for expanded AgX semiconductors.

central anion (4-coordinate $r_{Na^+} = 1.13$ Å, $r_{Ag^+} = 1.14$ Å).[7] At silver concentrations at which most cages contain at least one Ag^+ ion, additional silver results in weakening of the Ag–X bond, preventing further contraction of the unit cell. In the case of Na^+ far-IR absorptions, at lower concentrations the translatory frequency remains essentially constant, but it decreases at higher concentrations when the proportion of cages containing more than one Ag^+ increases. Our present hypothesis is that at low concentrations the AgBr molecules act as isolated defects having no effect on the Na^+ translatory vibrations. Above percolation threshold loadings, the Ag^+ ions must be considered part of the whole unit cell for the vibrational problem, and, because of their weaker interaction with the support compared to sodium, reduce the vibrational frequency of the Na^+ modes.

UV–visible reflectance spectra of Na,Ag,Br–sodalites obtained at various silver loadings show a continuous growth of components at 245–255 and 300–320 nm as the silver concentration increases (Figure 2), corresponding to the $(4d^95s)^1D,^3D \leftarrow (4d^{10})^1S$ excitations of the Ag^+ in $(Na^+)_n(Ag^+)_{4-n}Br$ moieties, respectively. At low Ag^+ loadings, the transitions are similar to the gas-phase values of 230 and 320 nm for the AgBr monomer.[8] In many other host matrices containing quantum-size particles, an increase in the loading of the semiconductor material results in a red shift as the particle size increases.[9] Inside the sodalites, the I–VII cluster nuclearity is limited to five, and no significant absorption (excitation, $\lambda_{em} = 580$ nm) band shifts occur at higher loadings for the Cl^-,Br^- series, in contrast to the I^- series. This difference appears to originate in the more pronounced Ag^+ ion loading sensitivity of the sodalite unit-cell dimensions (inter-β-cage distances and coupling) for the iodide series ($\Delta a_0 = 0.06$ Å) compared to the chloride and bromide series ($\Delta a_0 = 0.02$ Å). Even after complete silver exchange, the absorption edge remains at higher energy than in bulk AgBr. As in the bulk silver halides, the band positions show a halide dependence. A red shift is observed for the bigger anions in larger unit cells in the case of the isolated molecular and fcc bulk[10] forms of the silver halide. The *amonotonic* behavior of the estimated absorption edge[11] for the expanded silver halides is indicative of an interplay of decreasing band gap with decreasing bandwidth down the halide series, implying that the extent of inter-β-cage coupling follows the order of the observed distances between the centers of β-cages, i.e., Cl < Br < I (Figure 2k).

This investigation shows that an organized assembly ranging from isolated molecules to expanded structures stabilized inside a sodalite host matrix can be readily fabricated of a material that is normally a I–VII semiconductor. These materials may be suitable for the chemical synthesis of monodispersed nanostructures, of interest in quantum electronics and nonlinear optics.

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Supplementary Material Available: Details of the synthesis of sodium–sodalites and silver–sodalites and tables of crystallographic data for NaAgBr–SOD, AgBr–SOD, AgCl–SOD, and AgI–SOD (3 pages). Ordering information is given on any current masthead page.

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Heterosite Reactivity of Linked Bis(μ-phosphido)-Bound Isostructural Co_xMo_{4-x} Clusters (x = 2, 3). Characterization and Reactivity of a Novel μ_4-η^2-NO Cluster[1]

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Interest in the reactivity of heteronuclear clusters arises from the possibility of site selectivity induced by a particular metal, and novel reactivity patterns via cooperative effects between metal centers.[2] An isostructural array of bimetallic clusters that differ only in their metal–metal ratios might yield insight into the synergistic effects of heteronuclear interactions.[3] In order to study the effects of changing the metal–metal ratio in a series of heteronuclear clusters, we have synthesized and fully characterized a partial family of tetrahedral molybdenum–cobalt clusters that

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