may represent *dynamically* interconverting conformational substates. The simplest mechanism that incorporates this suggestion and satisfactorily describes the present data includes three such substates (Scheme II). In this mechanism, the ^{3}(ZnP) → Fe^{3+}P ET reaction occurs only within one form, B, of A* to produce the corresponding form of I. This substate, I_B, undergoes rapid ET to regenerate A, but it is not the most stable form of I and concurrently rearranges to two substates, I_C and I_D,[15] that are more stable but much less reactive. Experiments are now in progress to test this and other models, to examine whether the suggested conformational changes are interfacial or intraprotein,[13d] and to explain the sharply different values of k_b among the conformational substates of the complex.

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(15) The microscopic rate constants for Scheme II are obtained from the fits to the kinetic progress curves (Figure 1 and footnote 7) as follows; $k_{bB} \sim f_1k_1$; $k_{dC} \sim f_2k_1$; $k_{dD} \sim f_3k_1$; $k_2 \sim k_{bC} + k_{uC}$; $k_3 \sim k_{bD} + k_{uD}$. Setting $k_{uC} \sim k_{uD} \sim 0$ gives the lowest value for the ratio of ET rate constants: $k_{bB}/k_{bC} \approx k_1/k_2$ and $k_{bB}/k_{bD} \approx k_1/k_3$.

A Very Large Calcium Dialkoxide Molecular Aggregate Having a CdI_2 Core Geometry: $Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2$

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Herein we describe the first molecular calcium dialkoxide.[1] The aggregate size exhibited by the title compound is among the *largest* known for alkoxide complexes,[2] yet demonstrates Bradley's classic structural theory[3] which states (in part) that metal alkoxides will adopt the *smallest* degree of aggregation that permits the metal atoms to attain their preferred coordination numbers. The structure of $Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2$ (**1**) helps to rationalize the general properties of group 2 alkoxides.

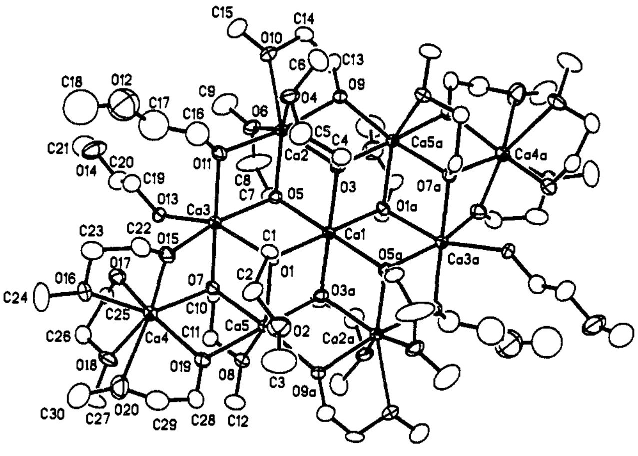

Figure 1. ORTEP of $Ca_9(OCH_2CH_2OMe)_{18}(HOCH_2CH_2OMe)_2$ (**1**). Average distances (Å): Ca–(μ_3-O), 2.390 (8); Ca–(μ_2-O), 2.291 (8); Ca–O_{ether}, 2.60 (1). Other distances (Å): Ca(3)–O(13), 2.455 (7); Ca(4)–O(17), 2.313 (9). The longer Ca(3)–O(13) separation likely pertains to the 2-methoxyethan*ol* ligand.

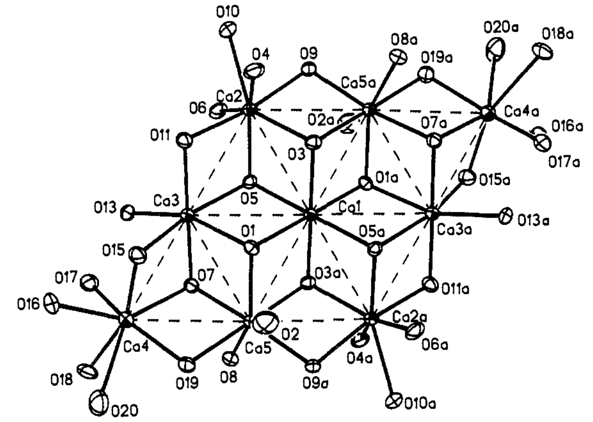

Figure 2. View of the central $Ca_9(\mu_3\text{-O})_8(\mu_2\text{-O})_8O_{20}$ core of **1**.

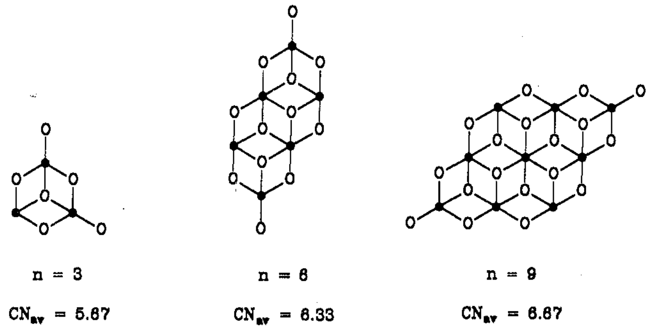

Figure 3. Sample calculations using a CdI_2-based model for $[Ca(OCH_2CH_2OMe)_2]_n$ oligomers having n = 3, 6, and 9. The small, filled circles represent calcium atoms and the larger, open circles represent alkoxide oxygen atoms of the 2-methoxyethoxide ligands. Note that each *ligand* also participates in one Ca–O_{ether} dative bond (not shown).

Compound **1** was prepared by interaction of calcium filings and 2-methoxyethanol (ratio 1.0 g atom to 2.5 mol, respectively) in refluxing hexane and was crystallized from the filtered reaction mixture as small needles (64% yield).[4] The molecular structure[5] of **1** (Figures 1 and 2) contains three 6-coordinate and six 7-coordinate calcium atoms for an average coordination number (CN$_{av}$) of 6.67. The central $Ca_9(\mu_3\text{-O})_8(\mu_2\text{-O})_8O_{20}$ core (Figure 2) mimics the layer structure of CdI_2 (except at the periphery) in that nine coplanar calcium atoms occupy octahedral holes between two close-packed oxygen layers. Significantly, the

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(1) Calcium *aryl*oxide complexes have been reported.[1a–c] Several recent studies claim to employ soluble calcium alkoxides; however, these substances are uncharacterized.[1d–f] (a) Hitchcock, P. B.; Lappert, M. F.; Lawless, G. A.; Royo, B. *J. Chem. Soc., Chem. Commun.* **1990**, 1141. (b) McCormick, M. J.; Moon, K. B.; Jones, S. R.; Hanusa, T. P. *J. Chem. Soc., Chem. Commun.* **1990**, 778. (c) Cole, L. B.; Holt, E. M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1997. (d) Hirano, S.; Hayashi, T.; Tomonaga, H. *Jpn. J. Appl. Phys.* **1990**, *29*, L40. (e) Nonaka, T.; Green, M.; Kishio, K.; Hasegawa, T.; Kitazawa, K.; Kaneko, K.; Kobayashi, K. *Physica C* **1989**, *160*, 517. (f) Kobayashi, T.; Nomura, K.; Uchikawa, F.; Masumi, T.; Uehara, Y. *Jpn. J. Appl. Phys.* **1988**, *27*, L1880.

(2) To our knowledge the largest structurally characterized molecular alkoxide aggregate is the cyclic decamer $[Y(OCH_2CH_2OMe)_3]_{10}$: Poncelet, O.; Hubert-Pfalzgraf, L. G.; Daran, J.-C.; Astier, R. *J. Chem. Soc., Chem. Commun.* **1989**, 1846.

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(4) Satisfactory elemental (C, H, Ca) and spectroscopic analyses were obtained. See the supplementary material.

(5) Crystal data for **1**: $C_{60}H_{142}Ca_9O_{40}$, M_r = 1864.5, triclinic, $P\bar{1}$, a = 10.220 (4) Å, b = 15.515 (5) Å, c = 15.991 (4) Å, α = 67.29 (2)°, β = 87.17 (3)°, γ = 80.98 (3)°, V = 2309.9 (13) Å^3, T = 295 K, Z = 1, D_{calcd} = 1.340 g cm^{-3}, λ(Mo Kα) = 0.71073 Å. Of the 8176 unique intensities measured, 3123 with $F_o > 6.0\sigma(F_o)$ yielded $R(F)$ = 0.0666 and $R_w(F)$ = 0.0354.

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nonmolecular compounds $Ca(OH)_2$,[6] $Mg(OH)_2$ (brucite),[6] $Ca(OR)_2$,[7] $Sr(OR)_2$,[7] and $Ba(OR)_2$[7] (R = Me, Et) all possess the CdI_2 structure.

In order to develop a reasonable structural model that correlates n and CN_{av} for various $[Ca(OCH_2CH_2OMe)_2]_n$ oligomer sizes, we make the following assumptions. First we assume that oligomers will adopt a CdI_2 core geometry. Thus, calcium atoms will arrange in a close-packed manner with each Ca_3 triangle capped by one μ_3 alkoxide, each Ca_2 edge bridged by one μ_2 alkoxide, and each remaining alkoxide occupying a terminal position. We also assume that each ether oxygen will participate in one Ca–O dative bond. We may then readily calculate CN_{av} as a function of n (see Figure 3). According to this model an aggregate with $n = 9$ produces a CN_{av} of 6.67, as was found in **1**, and as n decreases, so does CN_{av}. Similarly, as n increases above 9, CN_{av} increases above 6.67 (to a point).

Two opposing thermodynamic factors likely determine the observed aggregate size: (1) the enthalpic gains (per metal atom) resulting from coordinative saturation through internuclear bridge (dative-bond) formation and (2) the translational entropy losses (per metal atom) resulting from oligomerization. Typical coordination numbers for calcium(II) are 6–9, with 8 being most predominant.[8] Thus the n observed for **1** likely reflects a compromise between the preferences for a larger CN_{av} and for a larger number of independent particles. Because **1** is among the smallest aggregates able to satisfy the coordination requirements of calcium, Bradley's structural theory obtains.[9]

We propose that the competition between the enthalpic and entropic factors cited above provides the basis for Bradley's empirical argument.[3] Because the enthalpic benefits of forming internuclear dative bonds should drop off after the coordination requirements of a metal atom are satisfied, oligomerization should proceed only to the point of coordinative saturation. Thus, in cases uncomplicated by M–M bonds or directional M–L bonding such as the group 2 alkoxides, Bradley's theory should hold.

Soluble and volatile alkoxides of calcium(II), strontium(II), and barium(II) are presently sought for the preparation of high-T_c superconductors by sol–gel and CVD techniques.[1,10] However, group 2 alkoxides with conventional, monodentate alkoxide ligands are generally nonvolatile and poorly soluble in nondonor solvents,[11] probably as a result of nonmolecular, CdI_2-like structures.[7] Bidentate alkoxide ligands may reduce molecularities sufficiently to allow soluble derivatives (such as **1**) to be obtained. A simple extension of the reasoning above suggests that appropriate *tridentate* alkoxide ligands may produce molecularities as low as $n = 2$ (with a CN_{av} of 7.0), perhaps inducing volatility as well.

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Supplementary Material Available: Description of experimental details and listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** (14 pages); listing of observed and calculated structure factors for **1** (30 pages). Ordering information is given on any current masthead page.

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Carbene/Anion Complexes. Unusual Structural and Thermochemical Features of α-Halocarbanions in the Gas Phase

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Recent advances in experimental techniques for generating and detecting singlet carbenes have led to a wealth of new information concerning the structures, thermochemical properties, and reactivity of these important organic intermediates.[1-18] We recently

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