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Prediction of Fluxional Behavior for Sn_4^{2-} in Solution

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Investigations of four-atom metal clusters have revealed some systematic structural guidelines.[1] Homoatomic clusters with 22-valence (s + p) electrons are square planar[2,3] (e.g., Te_4^{2+}, Se_4^{2+}), while clusters with 20 are tetrahedral[4-6] (e.g., Pb_4^{4-}, Tl_4^{8-}, As_4). However, 18-electron systems have yet to be characterized. Recently ^{119}Sn NMR evidence has been obtained[7] suggesting the existence of the 18-electron cluster Sn_4^{2-}. Further, this experiment indicates that the tin nuclei are equivalent on the NMR time scale. Specifically, only one type of $^{119}Sn-^{117}Sn$ interaction is observed. Although a rigid tetrahedral structure meets this requirement, our calculations alternatively suggest fluxional behavior in the Sn_4^{2-} cluster. This behavior entails motion through three compressed tetrahedral (D_{2d}) and three elongated tetrahedral (D_{2d}) structures while maintaining a minimal D_2 symmetry. A preliminary X-ray structural determination[8] indicates the existence of a distorted tetrahedral structure for the anion in the salt $(2,2,2\text{-crypt-K})_2Sn_4$.

Effective (pseudo-) potential (ab initio) calculations involving 184 core electrons and 18 valence electrons were carried out on an Amdahl 470V/7 computer to determine the total valence energy E_{VT}[9] as a function of nuclear coordinates. Effective potential studies have given structures and force fields of clusters[10,11] and other molecules[12] of the quality expected for all-electron studies with similar basis sets. Recent papers show that structures of anions can be determined reasonably well with a minimal basis set in all-electron SCF calculations[13] or in the effective potential approximation.[14] In our calculations the method[15] followed that of another cluster study[10] (Te_4^{2+} with a 4-Gaussian fit to atom-optimized single-ζ STO's[16]) with the exception that the Sn core orbitals were represented by double-ζ STO's,[17] with each STO represented by a contracted set of 4-Gaussians.[18] In this prior study the Te_4^{2+} bond lengths were determined to within 0.06 Å of experiment and the correct structural symmetry (D_{4h}) was verified.

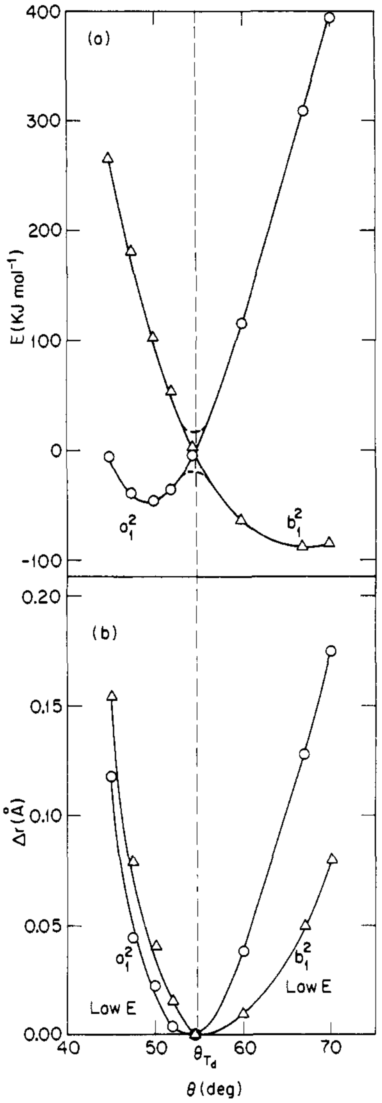

Figure 1. (a) Plot of $E_{VT}(a_1^2)$ (○) and $E_{VT}(b_1^2)$ (△) vs. θ. Points represent energies of structures at a given θ that have been separately optimized with respect to r. The zero of energy is taken to be the energy of the size-optimized tetrahedron. Dashed curves (---) show qualitatively expected behavior of a CI calculation near T_d. (b) Relationship between the values of Δr (Å) = (r − 1.998 Å) and θ.

Referencing the Sn_4^{2-} structure to T_d geometry and using spherical polar coordinates (θ, $\pi/4$), (θ, $5\pi/4$), ($-\theta$, $3\pi/4$), and ($-\theta$, $7\pi/4$), all with a common "radial" coordinate r, we calculated E_{VT} as a function of the polar angle θ. This displacement corresponds to an e-type bend. At each value of θ the "breathing" displacement r was optimized. We find (Figure 1a) two minima in $E_{VT}(\theta)$, a compressed tetrahedron at $\theta = 67°$ with $E_{VT} = -86.8$ kJ mol^{-1} relative to $E_{VT}(T_d)$ and an elongated tetrahedron at $\theta = 50°$ with $E_{VT} = -46.5$ kJ mol^{-1}. The energy of a D_{4h} structure ($\theta = 90°$) is found to be +46.2 kJ mol^{-1}. The Sn–Sn distances in Å are 3.11 (4) and 3.77 (2) at the compressed minimum (a puckered ring), 3.26 (6) at T_d, and 3.40 (4) and 3.10 (2) at the elongated minimum. These distances are somewhat larger than the average distances of 2.97 and 3.24 Å found experimentally[19] for the 16 short edges and 4 long edges, respectively, of the Sn_9^{4-} (C_{4v}) cluster. For Sn_4^{2-} in the solid, the observed distances average 2.96 Å, with a slight distortion toward C_{2v} symmetry.

The scale (r) optimized E_{VT} vs. θ curves shown in Figure 1a

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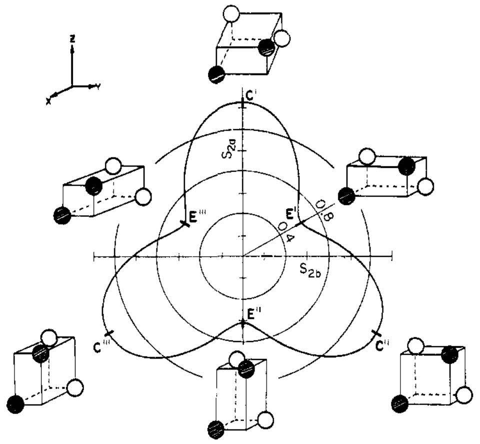

Figure 2. Plot of $\rho(\alpha)$ representing the shape of the minimum energy pathway in S_{2a}, S_{2b} (rad Å) vibrational space. T_d is at (0,0). C′, C″, C‴ are the compressed and E′, E″, E‴ are the elongated tetrahedra (D_{2d}). The space has a minimum symmetry of D_2. Square planes would be $\rho = 3.62$; $\alpha = 0, 2\pi/3, 4\pi/3$. The structures shown along the pathway contain an aribitrarily selected shaded pair of atoms in order to show the dynamical averaging.

represent two different electronic states. Relative sizes of the different electronic states of the cluster are shown in Figure 1b. Here we observe the participation of the totally symmetric stretch. For T_d Sn_4^{2-} the electron occupancy can be summarized as (inner valence)^{16} e^2. Distortion to D_{2d} symmetry breaks the e orbital symmetry down to a_1 and b_1, so that the energies plotted are for the states a_1^2 and b_1^2. These single-determinant spin singlets are degenerate for T_d symmetry but without "essential" configuration interaction (CI) do not represent either of the expected singlet terms (^{1}E and $^1A_1$) for this symmetry. Thus our method is incomplete for T_d symmetry itself. If the equilibrium geometry were tetrahedral, a paramagnetic $^3A_2$ ground term would be expected. However, there is no evidence of paramagnetism in solution,[7] suggesting a nontetrahedral species. Far from T_d symmetry the CI becomes less important and our single-determinantal description becomes valid.

Distortions of two other types were tried: (1) for a given θ, the azimuthal angle ϕ was increased for the two atoms above the x–y plane and decreased a like amount for those below it, reducing the symmetry to D_2 and (2) for a given θ the "radial" coordinates of an opposite pair of atoms were increased while those of the second opposite pair were decreased keeping the "edge lengths" constant (diamond-type bend for the square), reducing the symmetry to C_{2v}. The energy of the compressed tetrahedron specified above proved to be minimum with respect to these distortions, while the energy of the elongated tetrahedron was at a maximum with respect to the variation of ϕ.

In Figure 2 a fluxional pathway is represented by the trefoil $\rho(\alpha) = \rho_0 + \rho_1 \cos(3\alpha)$, where $\rho = (S_{2a}^2 + S_{2b}^2)^{1/2}$, $\alpha = \tan^{-1}(S_{2b}/S_{2a})$, and S_{2a} and S_{2b} are e-bending coordinates for a tetrahedron.[20] Constants ρ_0 and ρ_1 are obtained from the minimum energy compressed and elongated tetrahedra and are, respectively, 1.037 rad Å and 0.405 rad Å. Threefold symmetry in the S_{2a}, S_{2b} space (e-bend in T_d) requires the periodicity of the functional form of $\rho(\alpha)$. Further, the wave function changes smoothly from b_1^2 to a_1^2 as the metal cluster follows the motion through D_2 symmetry (as the phase angle α increases by π). Our calculated value of 40 kJ mol^{-1} for the barriers encountered along the pseudorotational pathway (Figure 2) falls below the minimum barrier height detectable by room-temperature NMR. Thus, per our calculations, there should be "effective" T_d symmetry, i.e., only one type of ^{119}Sn–^{117}Sn interaction.

We emphasize that while NMR evidence[7] is compatible with either statically or dynamically equivalent Sn–Sn pairs for Sn_4^{2-} in solution, the former explanation implying T_d symmetry, our ab initio study clearly supports the latter interpretation. The structural data[8] for the ion in the solid are characterized by substantial thermal parameters and thus may be compatible with, but do not confirm, our result that this 4-atom 18-valence electron cluster is more stable as a flattened tetrahedron of D_{2d} symmetry than as a regular tetrahedron or a square.

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Azidomethyl Phenyl Sulfide. A Synthon for NH_2^+

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The growth in the importance of direct metalation methods[1] creates a requirement for conjunctive reagents capable of directly combining with such organometallics. The importance of primary amines, both as synthetic intermediates and as entries into nitrogen heterocycles, led us to search for a source of NH_2^+ which could be introduced by a conjunctive reagent requiring nothing more than a hydrolytic workup.[2-4] Our work on α-sulfenylated alkyl azides[5] turned our attention to azidomethylphenyl sulfide (**1**). While azides bearing electron-withdrawing groups are facilely attacked by Grignard reagents at the terminal nitrogen to give triazenes, very few reports exist for alkyl azides in which the

$PhSCH_2N_3$

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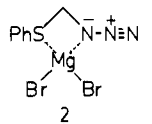

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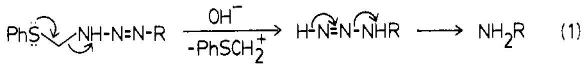

$$PhS\text{-}CH_2\text{-}NH\text{-}N{=}N\text{-}R \xrightarrow[-PhSCH_2^+]{OH^-} H\text{-}N{=}N\text{-}NHR \longrightarrow NH_2R \quad (1)$$

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