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First-Order Jahn−Teller Effect, Not Metal−Metal Bonding, Is Responsible for Structural Distortion in $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$ Excited States

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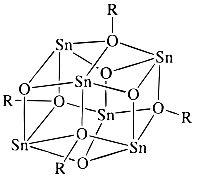
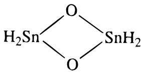
The photoluminescent properties of tetra- and hexanuclear clusters of transition and main group metals with d^{10} and s^2 electronic configurations, such as, for example, $[CuI(py)]_4$ (py = pyridine) and $[Tl(\mu_3\text{-}OMe)]_4$, respectively, have generated considerable interest.[1−3] Intriguingly, as the Stokes shift between the excitation and emission maxima for these clusters is routinely unusually large, the existing proposal is that their excited states are structurally distorted relative to their ground states by virtue of (enhanced) metal−metal bonding in the former that leads to a symmetric framework contraction.[1] Such a mechanism was proposed by Kunkely and Vogler[3] to account for the large Stokes shift of $\Delta\bar{\nu} = 13\,074$ cm^{-1} (1.62 eV) observed for the hexanuclear cluster, $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OMe)_4$ (**1**).[4] Unfortunately, for main group clusters, support for this hypothesis is rather tenuous as, to date, only very qualitative group theoretical arguments have been presented so far in its defense.[2,3] In addition, the question of metal−metal bonding between s^2 metal centers in such systems is still a topic of debate.[5,6] Thus, to address this key issue of electronic structure further, we undertook an ab initio study of the ground and excited states of $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ (**2**). Herein, we now report that a first-order Jahn−Teller (FOJT) effect,[7] and not metal−metal bonding, is most likely responsible for excited state structural distortion in this class of main group cluster. Given the fundamental nature of the principles underlying the FOJT mechanism, this finding serves to provide an important new model that may be used to rationalize the origins of similarly unique photophysical properties of other highly symmetric main group clusters as well.[2]



1: R = Me
2: R = H



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All geometry optimizations and CI singles (CIS) single-points were performed using Gaussian-94 with the LANL2DZ basis set, augmented by polarization and diffuse s and p functions.[8,9] Starting with the crystal coordinates for **1**,[4] further optimization of the singlet ground state at the RHF level of theory led to a T_d symmetric framework for **2** with structural parameters being in close agreement with those of the known derivative (see Table 1 and Figure 1). Most significantly, in neither structure do the tin−tin distances fall within the range expected for normal Sn−Sn bonding (e.g., 2.70−3.05 Å).[10] Furthermore, a "Atoms-in-Molecules analysis" of the gradient of the total electronic charge density, $\nabla(\rho)$, of **2** revealed that the nature of the critical point between any two adjacent tin atoms is characteristic of a (3,1) "ring" point, and this is indicative of a local depletion of charge that is associated with a lack of tin−tin bonding in the structure.[11] In addition, the density of ρ at this critical point is less than two-thirds the density found between the tin atoms in a similar analysis of $c\text{-}(H_2SnO)_2$ (**3**) which is not expected to possess tin−tin bonding and which also has a (3,1) point along the tin−tin axis. Thus, we find no evidence to support any degree of partial tin−tin bonding in the ground state of **2**. An analysis of Mulliken overlap populations for $Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$, as derived from extended Hückel approximate molecular orbital calculations, similarly failed to find any evidence for partial metal−metal bonding in this heavier atom analogue of **2**.[6]

The T_d ground-state electronic configuration for **2** ($^1A_1$) is characterized by a doubly degenerate HOMO and a triply degenerate LUMO with a gap of 5.47 eV. However, we find that the calculated oscillator strength for the LUMO ← HOMO transition in the T_d geometry is zero, thus indicating that the LUMO is of t_1 symmetry, thereby, making the transition formally forbidden.[12] Interestingly, the first allowed transition is to a higher energy triply degenerate orbital that generates a $^1T_2$ excited state which is 137.9 kcal mol^{-1} above the ground state as determined by the CIS method.[8] According to the Jahn−Teller theorem, however, a minimum for this resulting degenerate electronic state cannot exist as nuclear dynamics will lead to a structure of reduced symmetry in which the degeneracy is removed.[7] Satisfactorily, this anticipated FOJT effect for the excited state potential surface was quantitatively confirmed. Thus, to begin to model any geometric distortion that occurs upon excitation, the geometry of the ground-state triplet was optimized at UHF, leading, not to T_d, but rather, to a D_2 geometry (via a Jahn−Teller active vibrational mode to D_{2d}[12] followed by a slight twist of the framework) which proved to be the energy minimum on this potential surface. Next, taking the geometrical parameters of the D_2 structure as input, the first singlet excited state was optimized at the CIS level of theory by first manually breaking symmetry to C_2. This step is required as the gradient methods used cannot lose symmetry, only gain it. Optimization of this C_2 framework

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Table 1. Optimal Bond Lengths and Nonbonded Distances (Å) for the Lowest Energy Ground ($^1A_1$) and Excited ($^1B_1$) States of **2**

	2	**1**[a]
T_d ($^1A_1$)[b]		
Sn−O	2.068	2.05−2.08
Sn−OR	2.370	2.35−2.43
Sn···Sn[c]	3.515	3.51
C_{2v} ($^1B_1$)[b,d]		
Sn_1−O	1.965	
Sn_1−OH	2.105	
Sn_2−O	2.050	
Sn_2−OH	2.326	
$Sn_{3(5)}$−O, $Sn_{4(6)}$−O (short)[e]	2.037	
$Sn_{3(5)}$−OH, $Sn_{4(6)}$−OH (short)[e]	2.349	
$Sn_{3(5)}$−O, $Sn_{4(6)}$−O (long)[e]	2.060	
$Sn_{3(5)}$−OH, $Sn_{4(6)}$−OH (long)[e]	2.459	
Sn_1···Sn_2[c]	4.687	
Sn_1···$Sn_{3(5)}$, Sn_1···$Sn_{4(6)}$	3.467	
Sn_2···$Sn_{3(5)}$, Sn_2···$Sn_{4(6)}$	3.381	
$Sn_{3(5)}$···$Sn_{4(6)}$		

[a] Derived from crystal structure presented in ref 4. [b] See Figure 1 for structures. [c] Closest nonbonded distance. [d] $Sn_{3(5)}$ and $Sn_{4(6)}$ denote that each tin atom within the pairs, (Sn_3, Sn_5) and (Sn_4, Sn_6), is equivalent to the other by symmetry. [e] The short values are for O and OH groups that are bridging Sn_1 and $Sn_{3(5)}$ or Sn_1 and $Sn_{4(6)}$.

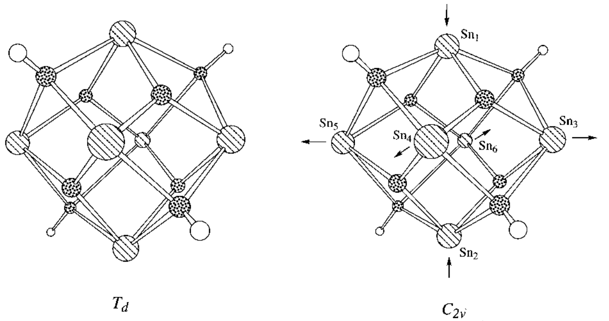

Figure 1. Comparison of the optimized ground-state T_d ($^1A_1$) and excited state C_{2v} ($^1B_1$) structures for **2**. For the C_{2v} structure, arrows qualitatively indicate the directions of nuclear displacements of the tin atoms from T_d symmetry.

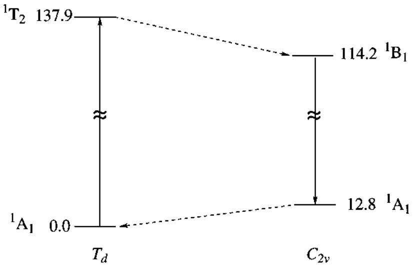

Figure 2. Schematic drawing of the relative energies (kcal mol^{-1}) for the ground and excited-state structures of **2** as discussed in the text. Solid arrows represent allowed electronic transitions and dashed arrows geometric relaxations.

then led to a C_{2v} geometry as the energy minimum rather than to either T_d or the initial D_2 structure (see Table 1 and Figure 1).[13] This excited $^1B_1$ state for the C_{2v} geometry was found to be 114.2 kcal mol^{-1} above the T_d ground state and 23.7 kcal mol^{-1} below the first allowed T_d excited state. It was next determined that the transition from this $^1B_1$ excited state to the C_{2v} ground state ($^1A_1$), which is 12.8 kcal mol^{-1} above the T_d ground state, is strongly allowed. However, the C_{2v} ground state does not represent an energy minimum on the potential surface, and as expected, optimization led directly back to the T_d geometry. These results are summarized in the schematic diagram of Figure 2, and they lead to a large decrease in energy from absorption to emission of $\Delta\bar{\nu} = 12\,762$ cm^{-1} (1.58 eV) for $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ (**2**), which is remarkably close to that observed for **1** experimentally.[3] Importantly, preliminary studies that are currently in progress also indicate that the degree of structural distortion and excited-state energies are sensitive to substituent effects, and this may provide a basis for fine-tuning the photophysical properties of $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$ derivatives.[14]

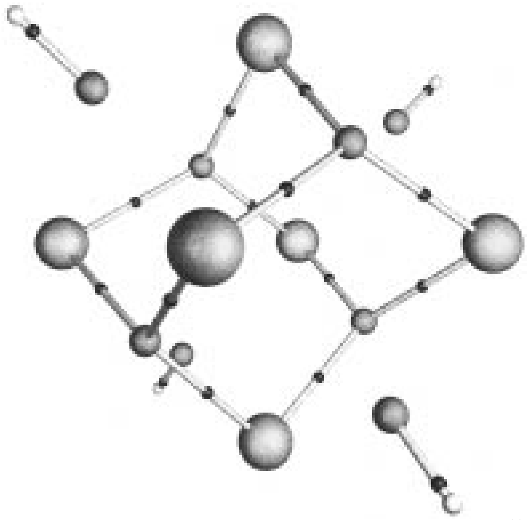

Figure 3. The molecular graph for the C_{2v} excited state of **2**.[11] Small black spheres represent the location of bond critical points between two atoms. Absence of bond paths between the tin atoms and the OH groups is indicative of either donor−acceptor or ionic bonding. Ring and cage critical paths have been omitted for clarity.

As a final consideration, the possible existence of enhanced metal−metal bonding in the excited states of **2** was investigated. The electronic configuration of the C_{2v} excited state is nondegenerate with the highest partially filled MO having considerable Sn−O antibonding character. In fact, the $C_{2v} \leftarrow T_d$ transition can perhaps be best described as being a metal-to-ligand charge transfer (MLCT) with significant charge density now residing on the oxygen atoms in the excited state relative to the ground state. Most importantly, analysis of $\nabla(\rho)$ for the first allowed singlet excited state in T_d revealed no change in the total density between any two adjacent tin atoms, which indicates that there is no enhancement of tin−tin bonding in this excited state relative to the ground state. When the same analysis was repeated on the ground and excited states of the C_{2v} structure, we also saw neither evidence of tin−tin bonding critical points (see Figure 3) nor a change in the density of ρ between the tin atoms in going from one state to the other. Thus, we conclude that, at the present time, there is little theoretical evidence for an increase in tin−tin bonding in $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$ derivatives upon excitation.

In conclusion, the present theoretical study provides strong support for a new model based on a FOJT effect that accounts for structural distortions associated with the excited state of the main group cluster, $Sn_6(\mu_3\text{-}O)_4(\mu_3\text{-}OR)_4$. Significantly, no evidence was obtained to support the prior hypothesis[1] that invokes metal−metal bonding in the excited state of these complexes. This new model may now also provide a better understanding of the role that substituent effects can play in controlling the photophysical properties of this novel class of photoemitter. Finally, given the T_d symmetry of the ground state of the tetranuclear thallium cluster, $[Tl(\mu_3\text{-}OMe)]_4$,[2,15] we feel that it is highly likely that an excited-state FOJT effect is operative in this system as well, and accordingly, a similar theoretical study is currently in progress.

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[13] The difference between the initial D_2 and final C_{2v} structures is exceedingly slight, differing in only a small asymmetric displacement of the two axial tin atoms.

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