Electronic control of the structural stability of quasiperiodic linear chains

Jeremy K. Burdett, University of Chicago
Gordon J. Miller, University of Chicago

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react as noted above. Second, if physical solution studies are transfer processes, and previous kinetic studies in this area indicate experimental notes. First, if a synthesis is being attempted and being made, care should be taken in the choice of buffers employed by two groups.20x21 We observe little difference in the synthetic procedure of Werner and Feenstra1 has been improved by two groups.20 We observe little difference in the synthetic utility of the compound prepared by either procedure, indicating that catalytic amounts of Co(II) are present when either method is followed. The solid complex is stable for months on the shelf.20

A major advantage in the use of this complex as a synthetic precursor is the rapid complex formation achieved at ambient temperatures with stoichiometric amounts of ligands and/or dilute solutions of ligands. The complex is also soluble in a wide variety of solvents, and synthesis is possible in any of these. The original synthetic procedure of Werner and Feenstra1 has been improved by two groups.20 We observe little difference in the synthetic utility of the compound prepared by either procedure, indicating that catalytic amounts of Co(II) are present when either method is followed. The solid complex is stable for months on the shelf.20

The more commonly used "tris(carboxylato)cobaltat(III)" complex is applicable to a wide variety of synthetic applications, but syntheses with this complex usually employ an excess of ligands, and removal of the third carboxylato group is often sluggish.22 Also, strictly nonaqueous preparations with this compound would be difficult since the complex is usually prepared just before use with aqueous hydrogen peroxide.22

This study has shown that the mode of rapid complex formation between this complex and ligands is undoubtedly via electron-transfer processes, and previous kinetic studies in this area indicate that the complex is a facile oxidant by either an inner-sphere14 or an outer-sphere15 route with many Co(II) complexes. For the inorganic chemist who wishes to employ this complex, the preliminary mechanistic studies reported here suggest two useful experimental notes. First, if a synthesis is being attempted and the reaction is sluggish, a trace of Co2+ should speed up the reaction as noted above. Second, if physical solution studies are being made, care should be taken in the choice of buffers employed unless the complex is completely free of Co(II).
representative chains. Certainly the critical observation is the definite level lies near the band gaps. We also note that the random chain the 13-atom chains will show regions of stability when the Fermi random, discussed in hand, the objectives of this preliminary account include understanding the energetic preference for a given structure as a function of band filling as well as given some insights into their eigenvalue spectra.

Before we examine the computational results, three points concerning our method need to be discussed. In the first case, since no analytical forms for the energy bands of the Fibonacci chain or any random system exist to date, the chains were limited to finite length. While the largest chain length studied included 300 orbital sites, we found that \( \sim 100 \) atoms provided sufficient information. Second, to minimize any edge effects from the terminated chains, the first and last members were linked within the Hamiltonian: a Born–von Karman boundary condition. The third point concerns the resonance integrals, \( \beta_{ij} \), between pairs of orbitals. These terms control the dispersion of the band but not the overall shape of the density of states. In order to compare the total energy for these model systems, we need some constraints on these interaction integrals. The method we selected maintained equal second moments, \( \mu_2 = \sum \langle E^2 \rangle \), among all systems, which is equivalent to setting the energy fluctuations for the models equal to each other.

In Figure 1 we illustrate the eigenvalue spectra of the representative chains. Certainly the critical observation is the definite series of band gaps appearing in the eigenvalue spectrum of the Fibonacci chain and the fractal nature of the level pattern itself. With respect to the periodic linear chain, the Fibonacci chain and the 13-atom chains will show regions of stability when the Fermi level lies near the band gaps. We also note that the random chain contains gaps in its spectrum similar to those of the Fibonacci chain. How can we easily understand these eigenvalues spectra? The translationally periodic 13-atom chains reduce the volume of the first Brillouin zone of the undistorted linear system by a factor of 13, thereby splitting the single band of the parent chain into 13 bands with gaps opening at \( k \approx (\pi/13a), (2\pi/13a), \ldots, (12\pi/13a) \). The integrated DOS (density of states) for each of these bands measures \( 1/13 \) the total integrated DOS for the parent chain. In addition to this expected pattern, case II exhibits four major band gaps: a consequence of the pseudopentagonal distortion of the parent chain as shown in 1. For any distortion of the periodic chain that retains translational symmetry, this analysis reproduces the qualitative features of the spectrum, but it is not adequate for the Fibonacci or the random chains.

An alternative approach, which is easily applied to systems without special translational symmetry properties, involves assembling the structure from molecular fragments. For the Fibonacci chain the two length scales \( L \) and \( S \) are associated with two resonance integrals, \( \beta_I \) and \( \beta_S \), in the Hamiltonian. Setting \( \beta_I \) to zero initially, we find the chain is composed of trimers and dimers of orbitals whose respective energy levels are well-understood from the solution of the square seeds of the allyl and ethylene units in organic chemistry. In units of \( \beta_S \), the trimer has energy levels at \(-21/2, 0, \) and \(+21/2\) while the dimer has levels at \(-1 + \pm 1\). Turning on the \( \beta_I \) interactions broaden these discrete, well-separated levels into bands as shown in Figure 1b. Therefore, we can determine the location of the band gaps for the Fibonacci chain by counting the number of trimers and dimers in the chain. For the infinite case, the ratio of the number of trimers to dimers is \( r:1 \). The integrated DOS for the five primary bands have the following relative magnitudes with increasing energy: \( r, 1, r, 1, \) and \( r \). The largest gaps occur at the band occupation of \( r + 1/3 = 1 - (2 - r) = 0.38196 \ldots \) and \( r - 1 = 1 - (2 - r) = 0.61803 \ldots \), at which we anticipate the greatest stabilization with respect to the linear chain. Since these argu-

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(9) Kadanoff, L., private communication.

ments apply to the other models as well, one can only comment on the gross features of the integrated DOS.

Before examining the structural stabilities, we also mention an alternative segmentation of the Fibonacci chain. From the opposite extreme, we can set $\beta_2$ to zero, which produces a chain of dimers (interaction integrals $\beta_1$) and isolated atoms. Upon introduction of the $\beta_2$ interaction, the initial "three-level" diagram expands to an eigenvalue spectrum with characteristics similar to those of Figure 1b. This viewpoint has some similarities to the soliton model in polymers.

We can depict the regions of stabilization for the various structural models by displaying the energy difference curves as a function of band filling. Figure 2 shows these curves with the periodic linear chain as the reference. The alternative structure has the lower total energy when the curve drops below $\Delta E = 0$. As predicted from its eigenvalue spectrum, the Fibonacci chain is clearly more stable than the present chain for the fractional band occupations, 0.382 and 0.618 ($2 - r$ and $r - 1$, respectively). However, by nature of the structure of the periodic alternative, case II, this chain and Fibonacci model are essentially isoenergetic.

The other periodic example III is not favored at these occupancies since the intrinsic connectivity is different: the dimers lie adjacent to each other. The random models never become the energetic preferences at the crucial occupations of 0.382 or 0.618. Thus, the Fibonacci chain possesses some intrinsic symmetry property that at certain electron counts favors it geometrical configuration over any random arrangement of orbitals. The important result of our calculation, placing the Fibonacci chain isoenergetic with a first-generation periodic one (albeit with a rather large lattice constant) allows direct comment on the feasibility of observing more examples of such species. The arrangement is clearly not a metastable curiosity but one that can energetically compete with periodic alternatives. It is in fact more stable than the simplest periodic chain of five atoms per cell with dimers and trimers.

We may view these energy difference curves using the language of moments. Energy difference curves as a function of electron count between the structural possibilities often have a characteristic shape determined by the order of the first disparate moment, $\mu_2(\rho)$, of their energy density of states. The energy difference curves for both the Fibonacci chain and the 13-atom chains are dominated by contributions from the fourth- and sixth-moment differences. Since the nth moment of a network is directly related to the number of walks of length n, beginning and ending at the same site, the qualitative similarities between the Fibonacci chain and the 13-atom chains derive from their essential connectivities. A detailed enumeration of the walks to second- and third-nearest neighbors, which we will report elsewhere, indicate the subtle differences between the two chains. The Fibonacci chain has smaller fourth and smaller sixth moments than any random arrangement of L- and S-length scales with the same ratio.

With a single orbital per site we are exclusively examining the effects of the intrinsic connectivity properties on the energy spectrum, and so our results will apply to many one-dimensional solids. Chemically realistic examples include polyacetylene, square-planar-coordinated platinum chains, and many of the organic metals involving planar organic units. The results suggest that under sufficient oxidation or reduction conditions, a quasi-periodic configuration for these one-dimensional systems is a possible reaction product. Note, however, that in order to achieve these critical band occupations for one-dimensional materials exhibiting quasi-crystalline states?

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Department of Chemistry
University of Chicago
Chicago, Illinois 60637

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Jeremy K. Burdett* Gordon J. Miller

Bromine Atom Abstraction from Aryl and Alkyl Bromides by the Triplet Excited State of the Tetraakis(µ-pyrophosphito)diplatinum(II) Tetraanion

Sir:

The tetraakis(µ-pyrophosphito)diplatinum(II) tetraanion, Pt4-

(µ3-P2O5H2)4Br4- has recently been the subject of several photochemical studies because of its having a long-lived phosphorescence at ambient temperature in aqueous solution. This triplet excited state is both a strong reductant and oxidant. Under photochemical conditions ($\lambda_{\text{exc}} < 350$ nm), we have recently found that the excited state reacts with alkyl andaryl bromides. For bromobenzene, the product complex $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2(\text{C}_6\text{H}_5)\text{Br}^-$ is that resulting from an oxidative addition reaction. For both bromopentafluorobenzene and 1,2-dibromoethane, however, the final product is $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^+$. It has previously been suggested that the mechanism of these reactions with alkyl and aryl halides involves a $S_{1/2}$ pathway with $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^+$ as reductant. This $S_{1/2}$ pathway is a stepwise electron-transfer mechanism leading to the formation of bromide ion and an alkyl or aryl radical. We have used transient difference spectroscopy to investigate the photochemical reaction of $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^+$ with $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{F}_5\text{Br}$, and several other alkyl and aryl bromides. In all cases the first detectable product is $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^-$. This mixed-valence $Pt(II)/Pt(III)$ intermediate shows a characteristic absorption band at 340 nm ($\epsilon = 5 \times 10^4$ L mol$^{-1}$ cm$^{-1}$) (Figure 1). We have confirmed this assignment by separately synthesizing $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^+$ by carrying out the biphononic photoionization of $\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_4$ in the presence of excess bromide ion (eq 1).

$$\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_4 + \text{Br}^- \rightarrow 2\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^- + \text{Pt}(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_2\text{Br}^- + (\text{e}^{-})$$

(1)

Laser (Nd-YAG at 355 nm) photolysis of aqueous methanolic solutions of $K[\text{Pt}3(\mu_3-\text{P}_{2}\text{O}_{5}\text{H}_{2})_4]$ containing either $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{F}_5\text{Br}$,

(1) Burdett, J. K.; Miller, G. J., to be submitted for publication.