

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 β_S to zero, which produces a chain of dimers (interaction integrals β_L) and isolated atoms. Upon introduction of the β_S 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 occupancies, 0.382 and 0.618 ($2 - \tau$ and $\tau - 1$, 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 occupancies 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 translationally 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 stable¹¹ 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, $\mu_n(\rho)$, of their energy density of states.¹² 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 n th 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,¹¹ 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 occupancies for one-dimensional materials dopant concentrations exceeding 20% are necessary. Examining two- and three-dimensional systems is an obvious extension of this analysis, as well as coloring the chains with different atomic species. Although known only for alloy systems at present, can we anticipate the possibility of one-dimensional materials exhibiting quasi-crystalline states?

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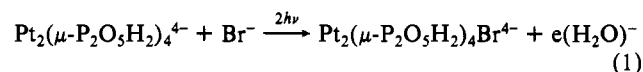
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Bromine Atom Abstraction from Aryl and Alkyl Bromides by the Triplet Excited State of the Tetrakis(μ -pyrophosphito)diplatinum(II) Tetraanion

Sir:

The tetrakis(μ -pyrophosphito)diplatinum(II) tetraanion, $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ has recently been the subject of several photochemical studies because of its having a long-lived phosphorescence at ambient temperature in aqueous solution.¹ This triplet excited state is both a strong reductant and oxidant.² Under photochemical conditions ($\lambda_{\text{max}} > 350$ nm), we have recently found that the excited state reacts with alkyl and aryl bromides.³ For bromobenzene, the product complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4(\text{C}_6\text{H}_5)\text{Br}^{4-}$ is that resulting from an oxidative addition reaction. For both bromopentafluorobenzene and 1,2-dibromoethane,⁴ however, the final product is $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$. It has previously been suggested that the mechanism of these reactions with alkyl and aryl halides involves an $\text{S}_{\text{RN}}1$ pathway with $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ as reductant. This $\text{S}_{\text{RN}}1$ pathway is a stepwise electron-transfer mechanism leading to the formation of bromide ion and an aryl or alkyl radical.⁵ We have used transient difference spectroscopy to investigate the photochemical reaction of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ with $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{F}_5\text{Br}$, and 1,2- $\text{C}_2\text{H}_4\text{Br}_2$. In all three cases the first detectable photoproduct is $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$. 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).⁶ We have confirmed this assignment by separately synthesizing $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ by carrying out the biphotonic photoionization of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ in the presence of excess bromide ion (eq 1).⁷



Laser (Nd-YAG at 355 nm) photolysis of aqueous methanolic solutions of $\text{K}_4[\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4]$ containing either $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{F}_5\text{Br}$,

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- (6) This extinction coefficient has been estimated from the ratio of the changes in optical density at 340 and 368 nm. The respective triplet state quenching rates for $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ with $\text{C}_6\text{H}_5\text{Br}$, $\text{C}_6\text{F}_5\text{Br}$, and 1,2- $\text{C}_2\text{H}_4\text{Br}_2$ in aqueous methanol are 1×10^5 , 2×10^7 and 8×10^6 M⁻¹ s⁻¹. These rate data were obtained from Stern-Vollmer plots.
- (7) Cho, K. C.; Che, C.-M. *Chem. Phys. Lett.* 1986, 124, 313-316. Roundhill, D. M.; Atherton, S. J. *J. Am. Chem. Soc.*, in press. $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ has also been prepared by the pulse radiolysis of aqueous solutions of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$ (Che, C.-M.; Gray, H. B.; Atherton, S. J.; Lee, W.-M., submitted for publication). In this work λ_{max} is observed at 370 nm. The difference in peak maxima arises because in our laser photolysis experiment we cannot subtract the contribution from the bleached band at 368 nm. In our uncorrected spectra, overlapping affects the observed peak maximum position of the absorption band of interest.

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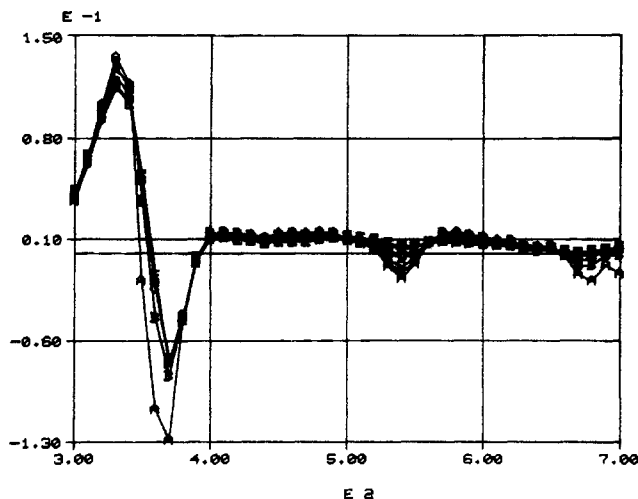
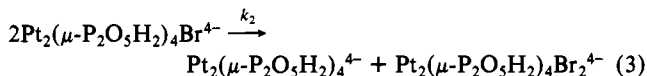


Figure 1. Transient difference spectra (absorbance vs. wavelength) for the laser pulse photolysis (Nd-YAG laser operating at 355 nm) of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and $\text{C}_6\text{F}_5\text{Br}$ in aqueous methanol. Time after pulse (μs): A = 0.1, B = 0.4, C = 1, D = 2.2, E = 6.5, F = 13.5.

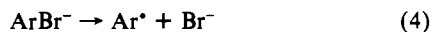
or 1,2- $\text{C}_2\text{H}_4\text{Br}_2$ gives, in each case, conversion to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ within 1 μs after the pulse (eq 2). The complex $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*} + \text{RBr} \rightarrow \text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-} + \text{R}^*$ (2)

$\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ then disproportionates to $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-}$ and $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}_2^{4-}$ with a second-order rate constant $k_2 = 9.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (eq 3).⁸ In each case we observe a rapid rise



in the 340-nm absorption band of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ to maximum concentration within 1 μs , and we detect no growth in this absorption band subsequent to the laser pulse.

It is particularly significant that $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4\text{Br}^{4-}$ is formed rapidly in the reaction with $\text{C}_6\text{F}_5\text{Br}$. Saveant has shown that there is an approximate linear correlation between the rate constant for halide ion cleavage from the haloaromatic radical anion and the standard potential of the aromatic halide.⁹ For bromobenzene ($E = -2.3 \text{ V}$ vs. SCE) we anticipate k_1 in reaction 4 to be ap-



proximately 10^8 s^{-1} , but for bromopentafluorobenzene ($E = -0.93 \text{ V}$ vs. SCE), we expect k_1 to have the much smaller value of 10^{-2} s^{-1} .^{10,11} Since our laser photolyses are carried out in solutions which have $[\text{C}_6\text{F}_5\text{Br}] \approx 10^{-2} \text{ M}$, this rate constant k_1 of 10^{-2} s^{-1} is some 8-9 orders of magnitude too slow for the $\text{S}_{\text{RN}}1$ pathway to be operative. The reaction with $\text{C}_6\text{F}_5\text{Br}$, therefore, follows a pathway analogous to that proposed for the reaction of $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{4-*}$ with isopropyl alcohol.³ Our results support a mechanism where the diradical triplet excited state abstracts a bromine atom directly from bromopentafluorobenzene.

For the case of $\text{C}_6\text{H}_5\text{Br}$ and 1,2- $\text{C}_2\text{H}_4\text{Br}_2$ the case is less clear. If, however, the $\text{S}_{\text{RN}}1$ pathway is followed, it is unlikely that diffusion outside the solvent cage occurs, especially since the final recombination step between $\text{Pt}_2(\mu\text{-P}_2\text{O}_5\text{H}_2)_4^{3-}$ and Br^- involves two negatively charged ions.

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Discrete Metal-Sulfide-Thiolate Complexes of an Early 3d Transition Metal

Sir:

We have recently initiated a program directed toward the development of discrete vanadium-sulfide-thiolate chemistry. Such work is designed to provide soluble mechanistic and structural models for polymeric vanadium sulfides, which, together with the sulfides of the other group 5 metals Nb and Ta, display interesting magnetic and electrical properties.¹ Of additional and particular stimulus to our work is the involvement of vanadium sulfides in crude oil refining. These sulfides act both as poisons of the Mo/Co hydrodesulfurization (HDS) fixed-bed catalysts² and also, because of their own intrinsic activity,³ as in situ generated HDS catalysts in a moving-bed system (the Aurabon process).⁴ Both of the above are particularly topical as the requirement to process the heavier crudes, which contain large amounts of vanadium, becomes necessary with increasing depletion of lighter crudes. In addition, of course, such studies should provide interesting comparisons with both 4d Mo/S and 5d W/S chemistry, which have been extensively explored.^{5,6} We herein report the preparation of some unusual and sulfur-rich products, which represent initial progress toward a better understanding of soluble V/S chemistry and which display features not seen in Mo or W chemistry.

Oxidation of V(III) by elemental sulfur in a reaction mixture comprising $\text{VCl}_3\text{:NaSPh:S:NET}_4\text{Br}$ in a molar ratio of 1:7:3:2 in MeCN^7 yielded an intensely dark green solution and some purple powder. After being stirred for 18 h, the reaction mixture was filtered and Me_3NBzI (2 equiv) added to the filtrate. The solution was refiltered and ether added to initiate the crystallization of $(\text{Me}_3\text{NBzI})_2[\text{VS}_2(\text{S}_2)(\text{SPh})]$ (1). After overnight storage, black well-formed plates were collected by filtration and washed with $\text{MeCN}/\text{Et}_2\text{O}$ (1:3).⁸ Yields are typically 30-40%. (With product identity established, we have employed a V:S ratio of 1:4, attempting to improve the yield, but instead obtained a completely different product currently under investigation. Consequently, we continue to employ the 1:3 ratio, which gives adequate yields reproducibly.) The structure^{9,10} of the anion of 1 is depicted in

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- (7) All reactions and manipulations were performed under an inert atmosphere employing freshly distilled solvents.
- (8) Complex 1 is soluble to any significant extent only in DMF in which it has limited stability. Anal. Calcd for $\text{C}_{26}\text{H}_{17}\text{N}_2\text{S}_5\text{V}$: C, 53.03; H, 6.33; N, 4.76; V, 8.65. Found: C, 53.60; H, 6.40; N, 4.85; V, 9.50.
- (9) Structures were solved by a combination of direct methods (MULTAN) and Fourier techniques and refined by full-matrix least squares.
- (10) Monoclinic space group $P2_1/n$, $a = 18.178$ (8) Å, $b = 8.843$ (2) Å, $c = 18.852$ (7) Å, $\beta = 107.06$ (2)°, and $Z = 4$, for 2807 unique data with $F > 3\sigma(F)$; non-hydrogen atoms were refined anisotropically, and hydrogen atoms were readily located and refined isotropically; final R (R_w) = 5.65 (5.63).

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