

Figure 1 shows that the temperature vs. chemical shift curves of the U(5) H-6 and H-5 of CAUGU are sigmoidal in nature and exhibit an upfield shift as the temperature is decreased. Such behavior is usually attributed to bases which are involved in hydrogen bonding. Although the dangling U does not base pair,<sup>14</sup> it is inherently associated with the duplex through its base-stacking interactions. It is likely, therefore, that it is experiencing the rapid conformational changes associated with both base stacking and duplex formation. Similar results were observed for the H-8 and H-2 resonances of the dangling A in CAUGA. This work clearly shows such base-stacking interactions between duplex and dangling base do exist, while the previous optical studies were only able to suggest the possibility of such an interaction. These results indicate the important role of base stacking in both duplex formation and duplex stability and they are fully consistent with the fine structural details of *t*-RNA<sup>Phe</sup> which have recently been elucidated by x-ray crystallographic analysis.<sup>15</sup>

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- (6) (a) M. C. Ganoza, A. F. Fraser, and T. Neilson, unpublished work. (b) Oligoribonucleotides are written in the normal 5'-3' sequence and the bases are numbered from left to right:  

CAUG	CAUGU	CAUGA
1234	12345	12345
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- (9) Melting temperature versus concentration data for these pentamers are not yet available, but data for AAGCUU,<sup>7</sup> GCUC:GAGC,<sup>10</sup> and CCGG<sup>11</sup> exists over the concentration range 10<sup>-5</sup> (UV) to 10<sup>-2</sup> M (<sup>1</sup>H NMR) and is consistent with the view that base paired duplexing is the only significant process occurring. Interduplex interactions appear to be negligible.
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## Reversible Binding of Dioxygen, Nitric Oxide, and Carbon Monoxide by Bis(3,5-di-*tert*-butylcatecholato)vanadium(IV)

Sir:

To gain insight to the properties and function of vanadocytes (cells found in the blood of Ascidians that contain high concentrations of vanadium(III)<sup>1-5</sup>), a study of model complexes has been undertaken. Although complexes of various catechols with vanadium have been prepared and studied previously,<sup>6-12</sup> few of the complexes have been isolated from solution and

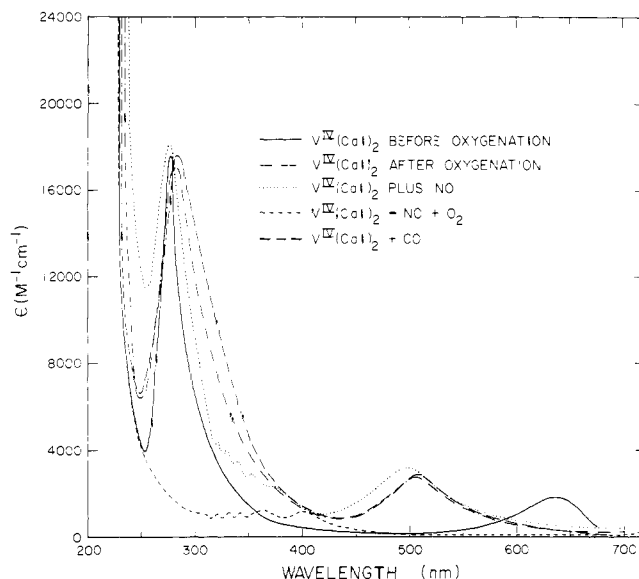


Figure 1. Absorption spectra for 2 mM bis(3,5-di-*tert*-butylcatecholato)-vanadium(IV) in methanol and for the adducts formed by O<sub>2</sub>, NO, and CO when present at 1 atm.

characterized. During the course of the preparation of the vanadium complexes that are formed by 3,5 di-*tert*-butylcatechol, the bis(catecholato)vanadium(IV) complex (**1**) has been isolated. We wish to report the reversible formation of O<sub>2</sub>, NO, and CO adducts with **1** in methanol and dimethyl sulfoxide solutions.

When vanadyl acetylacetonate (0.26 g, 0.001 mol) in methanol is combined with a solution of 3,5 di-*tert*-butylcatechol (0.44 g, 0.002 mol) in methanol under an inert atmosphere (argon), a green solution forms initially, which becomes blue on standing. Exposure of this blue solution to oxygen yields a deep violet colored species. The violet solution is reconverted to the blue form by deaeration with argon for 20 min. This cycle between the two species can be repeated by alternately bubbling argon and oxygen through the solution. Kinetic and equilibrium measurements are in progress. However, the initial results indicate that the formation of the O<sub>2</sub> adduct at 25 °C in Me<sub>2</sub>SO has a *P*<sub>1/2</sub> value of 33 Torr.

Further evidence for the formation of an O<sub>2</sub> adduct is provided by the IR spectrum for the purple species, both in CHCl<sub>3</sub> solution and in the solid state (KBr disk). Bands are observed at 1135 and 890 cm<sup>-1</sup> which are consistent with vibrations that are attributable to a superoxo and a peroxo formulation, respectively.<sup>13</sup> These bands are not observed for **1** or for the NO and CO adducts. The presence of both bands for the O<sub>2</sub> adduct indicates that the purple species probably is a peroxo-bridged dimer which results from an initially formed 1:1 vanadium-dioxygen adduct. Alternately, there may be an equilibrium between the two forms. Kinetic studies that are in progress support the postulate of a two-step adduct formation process.

The unoxxygenated (blue) species has been isolated by evaporation of the solution to a small volume, whereupon a dark blue-black precipitate is formed.<sup>14</sup> The complex also can be prepared in Me<sub>2</sub>SO, and vanadyl chloride or vanadyl sulfate can be used in place of vanadyl acetylacetonate. On the basis of the elemental analysis for the complex, the two catechol ligands apparently form a four-coordinate array about the vanadium(IV) center. Evidence for a symmetric tetrahedral coordination geometry around the vanadium is provided by EPR spectroscopy, which yields an isotropic eight-line spectrum, centered at a *g* value of 1.98, 805 G wide and with a peak-to-peak separation of 107.8 G (frozen Me<sub>2</sub>SO solution at liquid nitrogen temperature). An EPR spectrum is not ob-

served for the corresponding oxygenated species. The NO adduct in frozen Me<sub>2</sub>SO yields a complicated EPR spectrum that is consistent with the patterns that have been observed for square-pyramidal geometry. From the hyperfine splittings the adduct bonding appears to be to the N of an axially symmetric nitric oxide ligand.

The 2:1 ligand-to-metal stoichiometry of the product from the reaction under argon has been confirmed by a spectrophotometric titration. The UV-vis absorption spectra for **1** and for the adducts that are formed by O<sub>2</sub>, NO, and CO are illustrated in Figure 1. An absorption band at 750–800 nm is attributed to a semiquinone contaminant, while the band at 400 nm is due to a green species which results from further oxidation of the catechol. When the solutions of the NO and CO adducts are exposed to O<sub>2</sub>, they decolorize to yield pale yellow solutions. The purple color of the NO adduct can be regained by purging the solution of oxygen and reintroducing NO. This cycle can be repeated several times without apparent decomposition of the vanadium complex.

The loss of color on exposure of the NO adduct to oxygen indicates that the vanadium undergoes oxidation. Regeneration of the purple species by NO addition implies that the vanadium is reduced to the +4 oxidation state by NO. Thus, by this cycle the complex appears to have a catalytic effect on the oxidation of NO.

Perhaps the most interesting characteristic of **1** is the apparent tetrahedral geometry of the catechol oxygens around the vanadium(IV) center. This conclusion is supported by the infrared spectrum for **1**, which does not have a V=O stretching band in the 950–1050-cm<sup>-1</sup> region.<sup>15</sup> Hence, **1** is unlike the bis(acetylacetonato)oxovanadium(IV) complex, which does exhibit this characteristic stretching frequency because of its axial oxygen. Apparently the more basic character of the catechol ligands enhances their coordination to cause the displacement of the axial oxygen. Indeed, the increased coordination strength of the catechols to the vanadium is reflected by the V—O stretching frequency in the far-infrared region: 504 compared with 480 cm<sup>-1</sup> for vanadyl acetylacetonate<sup>15</sup> and 463 cm<sup>-1</sup> for VO(acac)<sub>2</sub>(py).<sup>16</sup>

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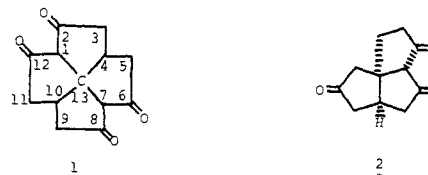
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## Synthesis of a Tetraketone of the Tetracyclo[5.5.1.0<sup>4,13</sup>.0<sup>10,13</sup>]tridecane ("Staurane") Series

Sir:

Recent interest in cyclopentanoid ring systems has been well documented,<sup>1</sup> and a number of them have been synthesized; triquinacene,<sup>2</sup> peristylane,<sup>3</sup> and the compounds of this type obtained by Paquette et al.<sup>4</sup> may serve as examples. The discovery of natural compounds with ring structures based in part (retigeranic acid<sup>5</sup>) or entirely (hirsutic acid,<sup>6</sup> the coriolins,<sup>7</sup> and isocomene<sup>8</sup>) on cyclopentanoid systems has stimulated additional interest in this area of research.



We wish to describe a simple synthesis of the tetraketone **1** from readily available starting materials. To the best of our knowledge, **1** is the first representative of the tetracyclo[5.5.1.0<sup>4,13</sup>.0<sup>10,13</sup>]tridecane series and we propose the name "staurane" (from Greek stauros, cross) for this highly symmetrical cyclopentanoid ring system.

Much of the synthetic work cited in ref 1–4 has been directed toward very specific targets. In contrast, our own efforts in this field<sup>9</sup> have been concerned with a general method: reaction of dimethyl 3-ketoglutarate with 1,2-dicarbonyl compounds. This reaction is a convenient source of enolic β-keto esters derived from bicyclo[3.3.0]octane-3,7-dione;<sup>9,10</sup> moreover, this methodology has recently been employed<sup>11</sup> to prepare the tricyclic triketone **2**, the parent ring system of isocomene,<sup>8</sup> and a modification has now permitted the synthesis of **1**.

Initially, several routes to **1** were considered, including conversion of the triketone **2** to **1**; however, these were cast aside in favor of a pathway which would take advantage of the C<sub>2v</sub> symmetry inherent in the tetraketone **1**. The immediate goal, therefore, was preparation of the diacid **9** which was accomplished with remarkable ease from benzyl acetoacetate **3**, as illustrated in Scheme I. Dialkylation of the ester **3** with

## Scheme I

