centrations in dimeric sites which make step 3 exceedingly rapid. The shift in the equilibrium or rather in the pH dependence of the equilibrium[16] is probably somewhat more complicated; however, a partial explanation may lie in the difficulty of dissociation and/or nucleophilic attack on protonated dimer. In summary, these results indicate that the monolayer environment produces a striking alteration of both rate processes and equilibria in this bimolecular reaction of metalloporphyrins. It will be important to investigate a variety of systems to determine whether in membranes or similar environments the attainment of high local concentrations by such packing phenomena or related interactions[17] may influence or promote the occurrence of reactions not occurring in solution, thus providing a mechanism for biological catalysis.

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(14) The pressure-area isotherms were measured on mixed films since films of pure 1 were somewhat unstable and subject to collapse.
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Intervalence (Charge-Transfer) Bands in Symmetrical and Unsymmetrical Bispyridinium–Pyridinyl Radical Complexes, $(\mathrm{Py}\cdot)_3{}^{2+}$

Sir:

Inorganic complexes between species which differ by one electron have been studied intensively.[1] More recently, organometallic complexes (biferrocene (II, III),[2] bisruthenium-pyrazine (II, III),[3] etc.) have provided further insight into the ground state and spectroscopic behavior of such complexes.[4] One small, but important, group of organic materials which exhibit an intervalence ("charge-resonance") absorption is that of the $\mathrm{TCNQ}\cdot^-$ complexes, with at least two distinct classes: the 1:2, $(\mathrm{TCNQ})_2{}^-$, and 2:3, $(\mathrm{TCNQ})_3{}^{2-}$, complexes.[5-7] (A closely related complex which appears to exhibit the property is 2TTF·TCM).[8]

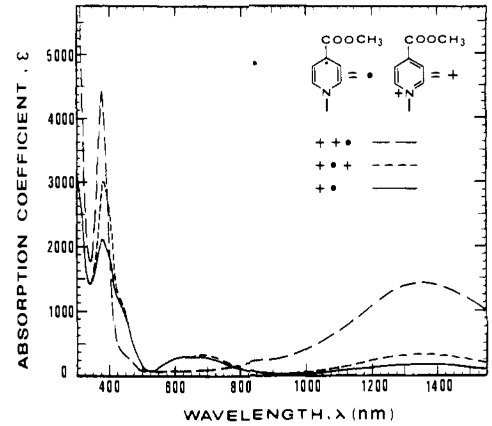
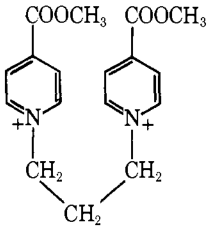
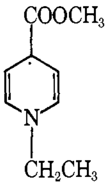


Figure 1. Absorption spectra for 1,1′-trimethylenebis(4-carbomethoxypyridinium) cation radical, (+·), $(\mathrm{Py}\cdot)_2{}^+$ (—); the symmetrical complex of the cation radical (+·) with 1-ethyl-4-carbomethoxypyridinium ion (+), $(\mathrm{Py}\cdot)^+$, written as (+·+) or $(\mathrm{Py}\cdot)_2{}^+{:}(\mathrm{Py}\cdot)^+$ or *sym*-$(\mathrm{Py}\cdot)_3{}^{2+}$ (- - -); the unsymmetrical complex of the biscation (++) with 1-ethyl-4-carbomethoxypyridinyl (·), (Py·), written as (++·) or $(\mathrm{Py}\cdot)_2{}^{2+}{:}(\mathrm{Py}\cdot)$ or *unsym*-$(\mathrm{Py}\cdot)_3{}^{2+}$, (- - - -). The visible absorption noted in the spectrum of the cation radical (+·) is assigned to the dimer of the cation radical.

We now report the observation of intervalence bands in complexes produced from (a) 1,1′-trimethylenebis(4-carbomethoxypyridinium) ion, $(\mathrm{Py}\cdot)_2{}^{2+}$, and 1-ethyl-4-carbomethoxypyridinyl radical (Py·), and (b) 1,1′-trimethylenebis(4-carbomethoxypyridinium) cation radical, $(\mathrm{Py}\cdot)_2{}^+$, and 1-ethyl-4-carbomethoxypyridinium ion, $(\mathrm{Py}\cdot)^+$.[9] The complexes are more stable than might have been anticipated, and the analogies to the TCNQ complexes are interesting and exciting.



$(\mathrm{Py}\cdot)_2{}^{2+}$



(Py·)

Pyridinyl radical[10] (Py·) in acetonitrile (6.4×10^{-4} M) was added in portions to a solution of $(\mathrm{Py}\cdot)_2{}^{2+}$ in the same solvent.[11] A new broad light absorption appeared at 1360 nm and reached maximum intensity (apparent $\epsilon_{\max}$ 1500) at a ratio if $(\mathrm{Py}\cdot)_2{}^{2+}$ to (Py·) of about 1:1. (A complete spectrum is shown in Figure 1.) Further additions of (Py·) caused a decrease in the intensity of the new band; at a reactant ratio of 1:2, the new band was almost gone.[12]

The "obvious" choice for the species responsible for the new band, the cation radical $(\mathrm{Py}\cdot)_2{}^+$, had been prepared and studied by Itoh[13] but the spectrum had not been measured past 700 nm. The cation radical was produced[13] and examined in both 2-methyltetrahydrofuran (MTHF) and acetonitrile solution. Only a small 1360-nm absorption could be found ($\epsilon \leq 100$) excluding $(\mathrm{Py}\cdot)_2{}^+$ as the species responsible for the new band. Furthermore, the ultraviolet absorption of the $(\mathrm{Py}\cdot)_2{}^+$ was lower in intensity and somewhat different in shape than that of the species associated with the new band, as the comparison made in Figure 1 shows.

The species responsible for the 1360-nm absorption was

Table I. Radical Complex Species, $P_n{}^{\pm y\,a}$ ($P = \mathrm{Py}\cdot$ = 1-alkyl-4-carbomethoxypyridinyl)

	y				
n	0	1	2	3	4
1	P	P^+			
2	P_2	$P_2{}^+$	$P_2{}^{2+}$		
3			$P_3{}^{2+}$		
4			$P_4{}^{2+}$	$P_4{}^{3+}$	
5					
6					$P_6{}^{4+}$

[a] The species described in the communication are isomeric forms of $P_3{}^{2+}$. Entries have been made in the table only for complexes for which there is some spectroscopic evidence.

established as a complex of two pyridinium rings and one pyridinyl radical by titrating the cation radical $(\mathrm{Py}\cdot)_2{}^+$ with pyridinium ion, $(\mathrm{Py}\cdot)^+$. Addition of the pyridinium ion caused the near-infrared band to increase in intensity (λ_m 1360 nm, ϵ_m 350) along with the ultraviolet band. The absorption curve at a 1:1 ratio of $(\mathrm{Py}\cdot)_2{}^+$ to $(\mathrm{Py}\cdot)^+$ was similar to but different from the curve observed for the combination of $(\mathrm{Py}\cdot)_2{}^{2+}$ and $(\mathrm{Py}\cdot)$ in intensity. For clarity and simplicity, we shall indicate the rings as either + or ·. Heating the solution of ++· for 18–20 h at 50–60° changed the absorption spectrum into that found for +·+, while heating the latter for many hours had no effect. Thus, the unsymmetrical complex is converted into the symmetrical complex by heating[14a] (eq. 1).

$$++ \text{ and } \cdot \rightarrow ++\cdot \rightarrow +\cdot+ \leftarrow +\cdot \text{ and } + \qquad (1)$$

The near-infrared transition is identified as an intervalence transition on the basis of (1) position and intensity, (2) band widths of ca. 3200 cm^{-1} (calculated for the high-temperature limit according to Hush,[1c] 4100 cm^{-1}), (3) substantial temperature sensitivities (thus, associated with a complex and favored by decreased relative motion of the components to a greater extent than local electronic transitions) (40% increase for ++·, ca. 20% increase for +·+ in $\epsilon_{\max}$ for a shift from +29 to −29 °C), and (4) similarity to bands noted for polyferrocene (nII, III) ions.[2a]

The ++· complex is produced in the same way from iodide, bromide, and perchlorate. A similar complex is formed from a biscation containing an *o*-xylylene group in place of a trimethylene group, but is not observed for a biscation connected by a tetramethylene group, implying that the complex requires rather precise orientation of the rings. The ++· complex is not stable if the acetonitrile is replaced by 2-methyltetrahydrofuran. The salt which separates is a mixture of both possible salts, the bissalt predominating because of solubility.

The cation radical $(\mathrm{Py}\cdot)_2{}^+$ itself dimerizes to yield either +·+· or +··+ which accounts for the weak intravalence absorption cited above. Itoh[13] noted the visible absorption at 77 K, but made no reference to its presence at 25 °C. It seems likely that the dimer is responsible for the low radical concentrations reported by Itoh, and that the dimer structure may be different in acetonitrile and methyltetrahydrofuran.[14b]

A summary (Table I) indicates that a number of relatively simple complexes and their surprisingly slow interconversions remain to be explored. A moderate number of analogous TCNQ complexes involving the neutral TCNQ molecules and the TCNQ·$^-$ anion radical could be listed in a parallel fashion, including (for T = TCNQ) T, T^-, $T_2{}^-$, $T_2{}^{2-}$, $T_3{}^{2-}$, and $T_4{}^{2-}$.[5,6] Relating the properties of such complexes to those of component species may be fruitful for the design of complexes with desirable solid-state properties, through the probable relationship between the occurrence of the IT bands and conductivity.

Kinetic studies on the interconversions of the complexes are possible,[14a] and it will be of special interest to probe possible differences between solids obtained from solutions containing different but isomeric complexes.

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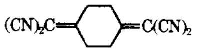

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(11) All solutions were prepared in all-glass apparatus and used after sealing off from a vacuum line. Bispyridinium salts were the gift of Dr. P. K. Huang. Spectroscopic measurements were made with a Cary 17 spectrophotometer.

(12) The properties of the $(\mathrm{Py})_2{}^{2+}$–$(\mathrm{Py}\cdot)_2$ solutions will be communicated separately.

(13) M. Itoh, *J. Am. Chem. Soc.*, **93**, 4750 (1971).

(14) (a) Detailed kinetic studies are under way. (b) Further details will be furnished with the related ++·· stoichiometry for the solutions noted in footnote 12.

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Synthesis of C-5 Substituted Pyrimidine Nucleosides via Organopalladium Intermediates

Sir:

We wish to report a facile method for the introduction of carbon chains at the C-5 position of pyrimidine nucleosides. We have found that substitution at the C-5 position of uridine and 2′-deoxyuridine may be effected by reaction of olefins with organopalladium intermediates generated in situ from mercurinucleosides.

Arylpalladium compounds (which may be prepared in