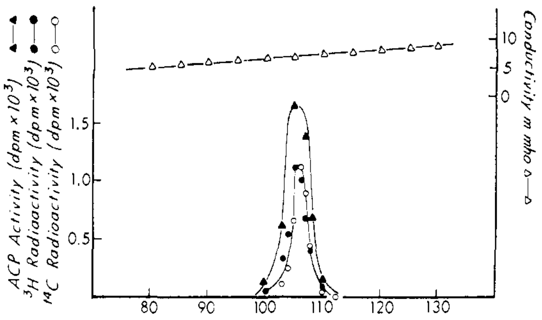

Figure 1. Identical samples of synthetic [$^3$*H*]holo-ACP were chromatographed separately on DEAE–cellulose columns (1) in the presence of authentic [$^{14}$*C*]pantetheine–ACP 1–74 and assayed for $^3$H and $^{14}$C radioactivity and (2) in the absence of carrier and assayed for $^3$H radioactivity and ACP activity.[9] The results of these experiments have been combined.

was eluted at the position expected for ACP. The deprotection was completed by hydrogenation of the sample at atmospheric pressure with palladium oxide on barium sulfate catalyst. The prosthetic group was then introduced enzymatically[8,17] to form holo-ACP which was then purified by ion exchange chromatography on DEAE–cellulose. (Yield of protein at this stage was 0.6%, based on the initial glycine value.)

The activity of the preparation was measured by two independent assays:[18] (1) the incorporation of $^3$H label into the synthetic product when the synthetic apo-ACP was treated with ACP synthetase and [$^3$*H*]pantetheine–CoA; and (2) the activity of the resulting synthetic holo-ACP in the malonyl pantetheine–$CO_2$ exchange reaction. The specific activities[19] in the two assays were found to be 33 and 30%, respectively, which indicated the presence of a large quantity of inactive material. It should be noted, however, that apo-ACP retained only 40% of its original activity when subjected similarly to HBr–TFA treatment and hydrogenation.

The synthetic product was found to cochromatograph with authentic 1–74 ACP[20] on ion exchange chromatography (see Figure 1) and gel filtration (Sephadex G-50).

Further work is now in progress to increase both the yield and specific activity of our preparation.

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(17) The enzyme, ACP synthetase, catalyzes the incorporation of 4′-phosphopantetheine according to the following reaction

$$\text{apo-ACP} + \text{CoASH} \xrightarrow{Mg^{2+}} \text{holo-ACP} + \text{adenosine } 3',5'\text{-diphosphate}$$

(18) It has been shown that at least two of the enzymes involved, ACP synthetase and β-ketoacyl ACP synthetase, show a high degree of specificity for ACP (see ref 6 and 7).

(19) Ratio of biological activity compared with authentic holo-ACP to the total protein as measured by the Folin–Lowry assay.

(20) [$^{14}$*C*]Pantetheine-ACP 1–74 was prepared by the digestion of [$^{14}$*C*]pantetheine–ACP with carboxypeptidase A (see ref 6 and 7).

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## A New Photosensitizer. Tris(2,2′-bipyridine)ruthenium(II) Chloride

*Sir:*

We have found that the cation $Ru(bipy)_3{}^{2+}$[1] photosensitizes the aquation of aqueous $PtCl_4{}^{2-}$. Previously, sensitized luminescence of transition metal complexes has been achieved using as donors organic molecules,[2,3] *trans*-$Cr(NH_3)_2(NCS)_4{}^-$[4] and $Ru(bipy)_3{}^{2+}$.[5] Organic donors such as various ketones and the acridinium ion have been found to sensitize the redox decomposition of Co(III) ammines[6] and the aquation of certain Cr(III) complexes[7,8] and of $Co(CN)_6{}^{3-}$;[9] biacetyl is reported to sensitize the aquation of $PtCl_4{}^{2-}$.[10]

The $Ru(bipy)_3{}^{2+}$–$PtCl_4{}^{2-}$ system is novel, however, in that it appears to represent the first case of a transition metal complex functioning as a photochemical sensitizer toward a second complex;[11] it may also represent the first example of energy transfer from a transition metal complex in room-temperature solutions. The spectroscopic properties of $Ru(bipy)_3{}^{2+}$ are such as to make this complex an unusually interesting and convenient sensitizer, and we wish here to propose its more general use.

The absorption and emission spectra of $Ru(bipy)_3{}^{2+}$ are shown in Figure 1. The prominent visible absorption feature is due to a spin-allowed charge-transfer (CT) process, and the emission arises from the lowest CT triplet state[12–14] at ∼17.8 kK. The phosphorescence lifetime in room-temperature aqueous solution is ∼0.7 μsec.[14] The intersystem-crossing yield is probably greater than 0.9[14–16] and the emission yield, even in fluid solutions, is relatively high. The complex is photochemically and thermally quite inert.

Preliminary experiments showed that anionic complexes such as $Cr(C_2O_4)_3{}^{3-}$, $Cr(CN)_6{}^{3-}$, $Co(C_2O_4)_3{}^{3-}$, and $PtCl_4{}^{2-}$ quench the phosphorescence in room-temperature aqueous solutions. In some cases precipitation occurs, however, and this observation plus the finding that cationic complexes do not quench well raise the possibility that the effect is a static one, quenching simply reflecting the presence of nonluminescent ion pairs. To test this question both luminescence and lifetime quenching studies were made, using $PtCl_4{}^{2-}$, with the results shown in Figure 2. The emission quenching was determined by means of an Aminco spectrofluorimeter and the lifetime quenching, on the same solutions, by means of a pulsed 337-nm $N_2$ laser (courtesy of Dr. J. H. Parks). The coincidence of the two sets of

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(1) bipy = 2,2′-bipyridine.

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(11) Reference 7 notes an at best marginally successful attempt to so use a Cr(III) complex.

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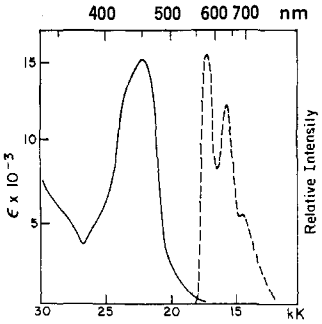

Figure 1. Room-temperature absorption spectrum (—) of aqueous $Ru(bipy)_3Cl_2$ and its corrected emission spectrum (---) at 77°K in an ethanol–methanol (4/1 v/v) glass.[15]

data in this Stern–Volmer plot establishes that the quenching is predominantly a diffusion-controlled process; static quenching would affect the intensity but not the lifetime. The Stern–Volmer quenching constant, $K_{SV}$, given by the slope of the plot, is $4.42 \times 10^3$ $M^{-1}$. The bimolecular quenching constant, $k_2$, is $6.5 \times 10^9$ $M^{-1}$ sec$^{-1}$ ($k_2 = K_{SV}/\tau_0$, our value for $\tau_0$ being 0.685 $\mu$sec), which is close to the diffusional encounter limit (see ref 17).

Sensitized reaction of the $PtCl_4^{2-}$ in deoxygenated $1 \times 10^{-3}$ $M$ $HClO_4$ was established as follows. Irradiated (450 nm) and dark solutions, after removing the $Ru(bipy)_3^{2+}$ with a cation exchanger, were compared spectrophotometrically. The spectral differences were consistent with the principal product being $PtCl_3(H_2O)^-$; the observed isosbestic points at 340, 370, and 420 nm are close to the reported ones at ~345, 380, and 428 nm.[18]

Kinetic evidence confirmed the product assignment. The second-order rate constant for $Cl^-$ anation of $PtCl_3(H_2O)^-$ (prepared by aging a solution of $PtCl_4^{2-}$) agreed within 5% with that measured, after removal of the donor, for a sensitized solution. From back-anation experiments, apparent aquation yields of 0.052–0.067 were obtained ($[PtCl_4^{2-}] = 1.6\text{–}1.7 \times 10^{-3}$ $M$, $[Ru(bipy)_3^{2+}] = 1.6 \times 10^{-4}$ $M$). Since the yield for disappearance of the donor (determined fluorometrically) is less than 0.01, a chemical sensitization path can essentially be ruled out.

The photochemical and quenching data give a limiting sensitized aquation yield of 0.07 ± 0.01. Reaction 3 of ref 6 may be written

$$T + C \xrightarrow{k_2} S + C^* \text{ or } C \qquad (1)$$

$$C^* \xrightarrow{\phi^*} \text{products} \qquad (2)$$

We conclude that $\phi^*$ is at least 0.07, a value substantially less than for direct photolysis of $PtCl_4^{2-}$ at 472 nm,[18] 0.17. Since the intersystem-crossing yield for $Ru(bipy)_3^{2+}$ is close to unity, possible explanations for the difference between the direct photolysis and the sensitized yields are the following: (a) process 1 may produce $C^*$ ~40% of the time, (b) the state $C^*$ and the one reached following 472-nm excitation may well be different and have different photochemical properties, (c) the aquation of $C^*$ may occur during the encounter lifetime and hence in an environment chemically different from that of $C^*$ as directly populated. Further experiments may allow some discrimination among these possibilities.

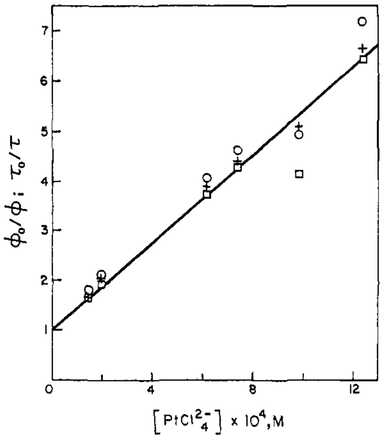

Figure 2. Quenching of the emission of $Ru(bipy)_3Cl_2$ in $1 \times 10^{-3}$ $M$ $HClO_4$ by $PtCl_4^{2-}$: +, lifetime data ($\tau_0 = 0.685$ $\mu$sec); ○ and □, relative intensity data taken before and after the lifetime measurements, respectively. $[Ru(bipy)_3^{2+}] = 3.4 \times 10^{-4}$ $M$ (deoxygenated).

In conclusion, we wish to emphasize that $Ru(bipy)_3^{2+}$ and analogous compounds exhibiting CT emissions[12,19,20] have much to recommend them as low-energy sensitizers in both organic and inorganic photochemical studies. The large extinction coefficients ($\epsilon > 10^4$) allow the use of low sensitizer concentrations and facilitate the detection of donor–acceptor chemical reactions. The intrinsic luminescences allow rapid visual detection of donor quenching; systems exhibiting no quenching need not be studied for sensitization. Molecular engineering, as by modifying the metal or the ligands, makes a wide range of donor triplet-state energies available;[21] and, of course, unlike many organic sensitizers, the complexes are water soluble. Finally, the remarkable ability of $Ru(bipy)_3^{3+}$ to exhibit chemiluminescence with various reductants[22] may be valuable to those wishing to probe the relation between photophysical processes and those of thermal reaction kinetics. It is possible, for example, that the mechanism of radiationless deactivation and of thermal activation is essentially the same.

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## 1,6-Diphosphatriptycene

*Sir:*

The preparation of heterocycles containing phosphorus has been the subject of numerous papers in