results may suggest the possibility that the heme methyl groups are misassigned and the field-dependent methyl resonance is the 5-CH_3 not the 3-CH_3. Clearly, more work on a number of cyto c^{III} with specific modifications around this region of the heme is in order.

The previously proposed[6] mechanism of electron transport via the heme edge suggests a possible biological relevance for this effect. Alternatively, the different conformations may play a role in the binding of the associated oxidase or peroxidase. Further characterization of this novel conformational flexibility and its kinetic and thermodynamic properties is in progress.

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Phillip D. Burns, Gerd N. La Mar*
Department of Chemistry, University of California
Davis, California 95616

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Simultaneous Emissions Including Intraligand Emission and Charge-Transfer Emission from $[Cu(PPh_3)_2(phen)]^+$

Sir:

Recently, there has been growing interest in metal complexes which exhibit multiple emissions which can be resolved spectrally and temporally. Several systems involving multiple intraligand excited states have been investigated[1] and more recently so have a number of d^6 complexes involving charge transfer (CT) excited states.[2-4] In the case of bis(1,10-phenanthroline)dichloroiridium(III), $Ir(phen)_2Cl_2^+$, emissions assigned to d-d and d-π^* states have been reported,[2] although the results regarding this system have been controversial.[2b,c] Another report has concerned the *fac*-$XRe(CO)_3$(3-benzoylpyridine)$_2$ systems where X is a halogen.[4] The latter systems appear to exhibit emission from d-π^* levels as well as from n-π^* levels of the bichromophoric ligand 3-benzoylpyridine. In the following, we report time-resolved studies of multiple emissions from the d^{10} system $[Cu(PPh_3)_2(phen)]^+$, where PPh_3 represents triphenylphosphine. Upon exciting this system at low temperatures, we have been able to resolve separate emissions with markedly different lifetimes and spectral properties.

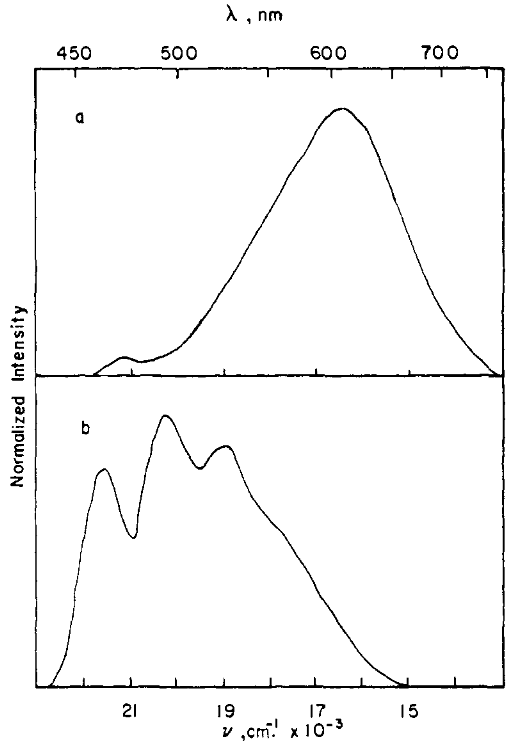

Figure 1. (a) The corrected, total emission spectrum of $[Cu(PPh_3)_2(phen)]^+$ at 77 K, exciting at 370 nm. (b) The corrected spectrum of the long-lived component of the emission detected through the phosphoroscope.

The complex was prepared from $Cu(PPh_3)_2NO_3$ as the nitrate salt by the method of Jardine.[5] Recrystallization from ethanol-water containing excess $NaBF_4$ afforded yellow crystals of the tetrafluoroborate salt. Microanalysis showed the complex to be a pure material. (Theoretical percentages: C, 67.40; H, 4.48; N, 3.28. Experimental percentages: C, 67.52; H, 4.32; N, 3.40.) A separate synthesis was carried out by reacting $[Cu(PPh_3)_4]BF_4$ with the phen ligand, and both preparations gave rise to the same emission spectra.

The emission spectra and lifetimes were measured using a 4:1 ethanol-methanol solvent. In the fluorimeter experiments the sample was immersed in liquid nitrogen, while in the laser experiments the sample was cooled to ~90 K using an Air Products cryostat. In either case the sample was cooled below the estimated glass transition temperature of 98 K.[6] In all experiments reported we used freshly prepared samples that had been deoxygenated by repeated freeze-pump-thaw cycles. The methanol (distilled in glass) was used directly as purchased from Burdick and Jackson. Troublesome solvent background emission from impurities in the ethanol was minimized by a careful fractional distillation at reduced pressure. The total emission spectrum was run on a SPEX Fluorolog spectrofluorimeter. The spectrum of the millisecond component, vide infra, of the emission was resolved on an Aminco-Bowman spectrofluorimeter using a phosphoroscope accessory. The instrument used to record the spectra of the shorter lived components will be described elsewhere.[7] Its source is a Phase-R N21K N_2 laser which gives 700-W (peak power), 5-ns (FWHM) pulses at a repetition rate of 30 Hz. The time capabilities of the laser apparatus were calibrated in a standard way using a Stern-Volmer quenching scheme.[8] Sample luminescence was focused through a Corning 0-52 filter (laser scatter attenuation ×1000) into a Jarrel Ash Model 82-405, ¼-m monochromator providing a 4-nm band pass. Emission detection was achieved by an RCA 1P28B photomultiplier specially wired for fast response.[9] Amplification and time resolution was achieved with a Tektronix Model 5S14N sampling oscilloscope for the nanosecond component and a PAR MODEL 162 boxcar integrator for the microsecond component. The lifetime of the phen ligand was measured in

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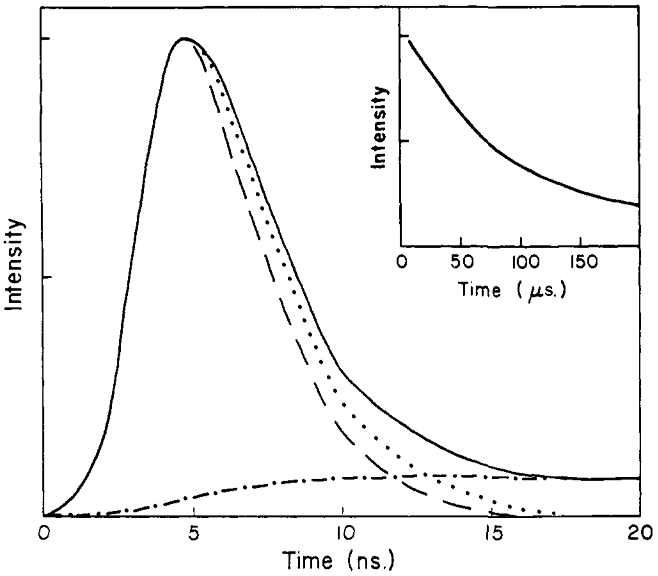

Figure 2. Time-resolved emission of the charge-transfer components: (---) instrumental pulse at 337 nm; (—) $[Cu(PPh_3)_2(phen)]^+$ emission at 570 nm; (-·-) calculated rise of the 115-μs component at 570 nm; (···) ≲1-ns component, resolved by substraction of the 115-μs component from the $[Cu(PPh_3)_2(phen)]^+$ emission at 570 nm.

the spectrofluorimeter using a guillotine shutter method. The lifetime of the millisecond component was measured by a variation on the method of Lewis and Kasha.[10]

The total emission spectrum of $[Cu(PPh_3)_2(phen)]^+$ in the alcohol glass at 77 K is presented in Figure 1a. The reported spectrum was obtained using 370-nm excitation, the wavelength maximum at 77 K of the d → π* charge-transfer absorption band of the complex. (Analogous charge-transfer bands have previously been characterized for complexes of this type.[11]) The total emission spectrum is characterized by band maxima at 465 nm (21 700 cm^{-1}) and 605 (16 500). Using a phosphoroscope accessory, the millisecond component of the emission was resolved from the total emission and is presented in Figure 1b. The shorter lived emission was examined using the laser apparatus and was found to decay in two stages (Figure 2). One component exhibits a lifetime of ≲1 ns, based on comparisons with convolutes of the instrumental pulse,[12] and the other exhibits a lifetime of 115 μs as determined from a standard log plot. The corrected emission spectra of the latter two components are presented in Figure 3. The spectrum of the ≲1-ns component was measured by scanning the emission monochromator, sampling at the time of maximum intensity of the laser pulse.[21] In an analogous fashion the spectrum of the 115-μs component was measured sampling 20 μs after the laser pulse.

All three components were observed for samples from either method of preparing $[Cu(PPh_3)_2(phen)]BF_4$, and the relative emission intensities did not depend on the method of preparation or on the length of time the solutions were exposed to light. Using the Aminco-Bowman and monitoring the sample emission at 580 nm, where the 115-μs emission dominates,[13] or selectively monitoring the millisecond component through the phosphoroscope at 462 nm, gave the same corrected excitation spectrum at 77 K down to the effective instrumental limit of 300 nm, and the excitation spectrum paralleled the absorption spectrum of $[Cu(PPh_3)_2(phen)]^+$. These findings strongly imply that the 115-μs and the 8.5-ms components stem from photoexcited $[Cu(PPh_3)_2(phen)]^+$. Since the laser source was not tunable, we were unable to measure the excitation spectrum of the weak ≲1-ns component which was only apparent on being time resolved from the 115-μs component.

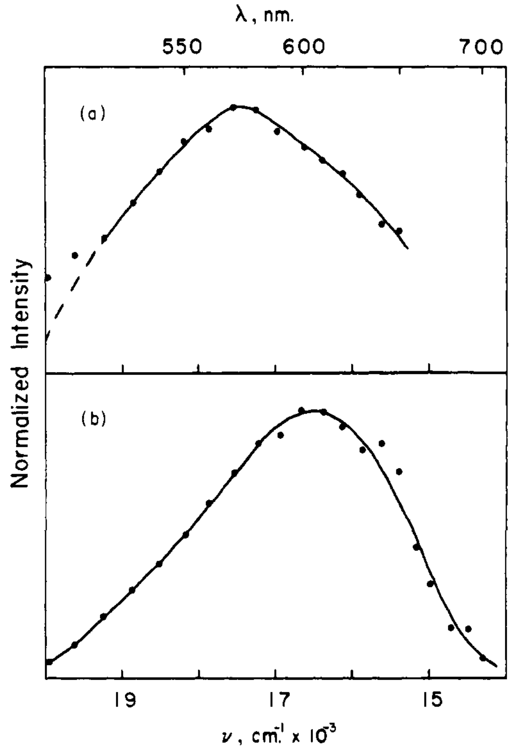

Figure 3. (a) The corrected emission spectrum of the ≲1-ns component.[21] A small contribution resulting from residual, higher energy, solvent impurity emission is apparent in the region of 500 nm. The dashed line approximates the sample contribution in this region. (b) The corrected emission spectrum of the 115-μs component.

Table I. Wavelength and Lifetime Data

system	wavelength maxima, nm	τ, s
phen[a]	459, 488, 521, 559	1.4 ± 0.1[b]
$[Cu(PPh_3)_2(phen)]^+$	461, 495, 526	8.5 ± 2.0 × 10^{-3} [b]
$[Cu(PPh_3)_2(phen)]^+$	608 ± 5	115 ± 12 × 10^{-6} [c]
$[Cu(PPh_3)_2(phen)]^+$	575 ± 10	≲1 × 10^{-9} [c]

[a] Wavelength maxima were taken from ref 14b. [b] 77 K. [c] ~90 K.

Compared with phen phosphorescence,[14] the structured, long-lived emission from the complex is slightly red shifted, differs somewhat in the vibronic detail, and is appreciably shorter lived; see Table I. Changes in energy, structure, and lifetime of these kinds are diagnostic of intraligand emission perturbed by coordination to a metal center.[15] Thus, the 8.5-ms component of the total emission spectrum of $[Cu(PPh_3)_2(phen)]^+$ is readily assigned as π-π* emission associated with the *coordinated* phen moiety. Conceivable origins for the 115-μs emission are an intraligand excited state of coordinated PPh_3, a d-π* state, or a metal-centered d-s excited state. An intraligand excited state of PPh_3 can be eliminated since it would exhibit emission at appreciably higher energies.[16] Although a d-s excited state cannot be ruled out, because of the low-lying charge-transfer band in the absorption spectrum, the 115-μs emission is most reasonably assigned to a d-π* state. The relatively long lifetime suggests that the state involved has triplet character. If so, then the complex exhibits simultaneous emissions from two separate triplet levels. This behavior is plausible because the d-π* state and the intraligand state are likely to be characterized by rather different geometries, since the intraligand state formally involves a Cu(I) center, whereas the d-π* state formally involves the Cu(II) center. In general, Cu(II) species are subject to the (pseudo)-Jahn-Teller effect and may be expected to be distorted considerably from the pseudotetrahedral configuration of the Cu(I) center. This being so, radiationless transitions between a vibrationallyrelaxed d-π^* level and a corresponding intraligand excited level would likely require activation and, as a result, could be inefficient in a low-temperature glass.

Like the 115-μs component, the $\lesssim$1-ns component exhibits a broad structureless spectrum.[20] In view of the relative energy and lifetime of the $\lesssim$1-ns component compared with the 115-μs component, it is tempting to consider that the former might be prompt fluorescence from the corresponding singlet d-π^* state.[17] However, because the $\lesssim$1-ns component is so weak and because its excitation spectrum has so far not been measured, an assignment would be premature.[19] Even if the component could confidently be associated with photoexcited $[Cu(PPh_3)_2(phen)]^+$, the singlet d-π^* assignment would not be unambiguous. Other possibilities would be a triplet d-π^* state involving another geometry and a triplet d-π^* species in another state of solvation.[3]

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(12) Actually, the comparisons indicated that the lifetime of the $\lesssim$1-ns component was ~500 ps, but, in view of the difficulties in accurately resolving such short lifetimes from an instrumental signal of this width, we are reporting the more conservative figure of $\lesssim$1 ns.
(13) We cannot specify the relative quantum yields of the $\lesssim$1-ns and 115-μs components with the data at hand, but it is apparent from the relative areas under the emission profiles in Figure 2 that the yield of the $\lesssim$1-ns component is considerably less than that of the 115-μs component.
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(17) Assuming this assignment, from the spectra in Figure 3 we would estimate that energy gap between the singlet and triplet dπ^* levels is ~1000 cm^{-1}—a figure which appears reasonable when compared with recent spectroscopic studies of $Fe(bipyridyl)_3{}^{2+}$.[18]
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(19) It can, however, be noted that the emission spectrum of the $\lesssim$1-ns component is quite distinct from those that would be observed for the obvious ligand redistribution products of the complex, i.e. PPh_3, Cu(I) complexes of PPh_3, and $[Cu(phen)_2]^+$.[11] However, other as yet unisolated complexes, e.g., $[Cu(PPh_3)(phen)(S)]^+$ where S is solvent, are conceivable derivatives and their presence in solution cannot be excluded at this point.
(20) Comparably short-lived emission has also been observed from bipyridyl analogues of $[Cu(PPh_3)_2(phen)]^+$.[11]
(21) In fact the spectrum obtained in this way also reflects a small contribution from the 115-μs component since the latter exhibits weak intensity at the time of the maximum in the laser output (Figure 2).

Michael T. Buckner, Thomas G. Matthews
Fred E. Lytle, David R. McMillin*
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

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Lanthanoids in Organic Synthesis. 5.[1] Selective Reductions of Ketones in the Presence of Aldehydes

Sir:

The central role of the carbonyl group in organic chemistry has generated substantial interest in developing methods that allow its selective reduction in the presence of other functional groups.[2] With several new reagents[3-10] a selectivity is observed that permits the reduction of aldehydes in the presence of ketones. In contrast, there is no efficient method for selectively effecting this type of reduction in the opposite sense, i.e., the reduction of a ketone in the presence of an aldehyde. Usually, this transformation necessitates a three-step process: protection of the aldehyde (e.g., ketalization), reduction of the ketone, and finally liberation of the aldehyde. Not only is a three-step process synthetically undesirable, but, in addition, the ketalization catalyst[11] is often not sufficiently selective, thus leading to low yields and/or separation problems.

We described in the previous paper of this series an approach for the simplification of this problem, based on the preferential *in situ* ketalization of aldehydes relative to ketones using a lanthanoid ion as the catalyst.[1] However, this method cannot be used with easily ketalized ketones.

We now report another solution to the problem which is an even easier and more attractive "one flask" method than the previous, achieving the desired selective reduction *without* the need for any stable, isolable protective group. Moreover, the scope of this method shows that it can be used in cases when the first method fails.

When an equimolar mixture of an aldehyde and a ketone in aqueous ethanol ($EtOH-H_2O$, 1:1.5) in the presence of cerium trichloride ($CeCl_3 \cdot 6H_2O$, 1 molar equiv), is cooled to −15 °C and treated with 1.5 molar equiv of $NaBH_4$,[12] a selective reaction occurs. The aldehyde is recovered almost quantitatively and the secondary alcohol is generated in high yield. The results given in Table I are illustrative of the selectivity that can be obtained by this process. With most nonconjugated aliphatic and alicyclic carbonyl compounds this selectivity is excellent. On the other hand, benzaldehyde and citral undergo substantial reduction under these conditions, results which suggest that sufficient selectivity cannot be expected with conjugated aldehydes. This observation, however, may be of synthetic value for it permits a discrimination in the reduction of aldehydes of various types. For instance, an equimolar benzaldehyde–hexahydrobenzaldehyde, when treated as above, affords benzyl alcohol in 85% yield and 98% recovery of hexahydrobenzaldehyde.

It is known that in general conjugated aldehydes are not hydrated and that nonconjugated aldehydes yield hydrates to a larger extent than ketones.[11] Thus, the efficient protection of the nonconjugated aldehyde function is most certainly achieved by the formation of a geminate diol. Hemiketal or ketal formation[1] can be excluded as the observed selectivity is almost the same (±5%) when the solvent is changed from ethanol-water to methanol- or 2-propanol-water. A second point is that the stability of the geminate diol is increased by Ce^{3+}. This effect was demonstrated for a mixture of cyclohexanone and hexanal. In a CD_3OD-D_2O solution, the NMR spectrum of this mixture exhibits no signal in the usual CHO resonance domain, suggesting that the aldehyde is totally converted into its hydrate. Reduction ($NaBH_4$, 1.5 equiv, −15 °C) yields cyclohexanol (100%), hexanol (49%), and hexanal (51%). The same reaction when performed in the presence of 1 equiv of $CeCl_3$ gives cyclohexanol (100%), hexanol (2%), and 98% recovered hexanal. The stabilization of the geminate diol under the reaction conditions was also tested with various ions (H^+, Cu^{2+}, Zn^{2+}, Ba^{2+}, Ti^{3+}, Cr^{3+}, Fe^{3+}), but they proved to be less effective[13] than Ce^{3+}. Thus, the effect of Ce^{3+} is large enough to ensure an adequate protection during the reduction