significantly different in the two electronic states. Quantum beats[17] should also be observable in the excitation and decay of triplet BP since the angle between the principal transverse axes of **D′** and the oxygen $2p_x$ and $2p_y$ orbitals is nearly 45°. And, finally, we note that there is no reason to suppose that orbital rotation is unique to this system; analogous behavior might be awaiting discovery in other aromatic carbonyls, N-heterocyclics, and a variety of transition-metal ions. Investigations of some of these systems are in progress.[18]

Registry No. BP, 119-61-9.

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Luminescence of a Series of Pentacarbonylpyridinomolybdenum(0) Complexes in Fluid Solution

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Of current interest is the photochemistry of substituted group 6B metal carbonyls having low-lying metal to ligand charge-transfer (MLCT) excited states.[1-7] Luminescence assigned to be from a low-lying MLCT excited state has been observed from complexes of the general formulas $M(CO)_5L$ and $M(CO)_4L_2$, where M = Mo, W, and L = *n*-electron donor, either in rigid glasses at 77 K[3,8] or in methane and argon matrices at 12 K.[9] The absence of literature reports concerning emission from group 6B carbonyl complexes in fluid solution has been attributed to the relatively high photoreactivity and efficient nonradiative decay of the excited states of these complexes. In this paper, we report electronic absorption, emission, and excitation spectra obtained from a series of $Mo(CO)_5L$ complexes in room-temperature solution. These complexes appear to represent the first class of molybdenum carbonyls that emit under fluid conditions.

Table I. Electronic Absorption and Emission[a] Spectral Features for $Mo(CO)_5L$ Complexes in Benzene at 298 K[b]

L	absorption max[c]	emission max, nm	emission half-width,[d] ×10³ cm⁻¹	emission quantum yield[e] ×10⁻⁴
4-ACpyr	394 (7650), ~440 (sh)	632	4.1	1.6
4-BNpyr	393 (7460), ~438 (sh)	647	3.7	4.3
4-CNpyr	392 (6300), ~435 (sh)	630	4.4	1.3
4-FMpyr	392 (5710), ~447 (sh)	668	3.8	1.9

[a] The excitation wavelength is 436 nm. Emission spectra were corrected for variation in instrumental response as a function of wavelength. [b] 8 × 10^{-5} to 2 × 10^{-4} M deaerated solutions. [c] λ, nm; (ε), M^{-1} cm^{-1}. [d] Width of emission band at half-height. [e] Relative to the luminescence of $Ru(bpy)_3^{2+}$;[14] accurate to within ±10%.

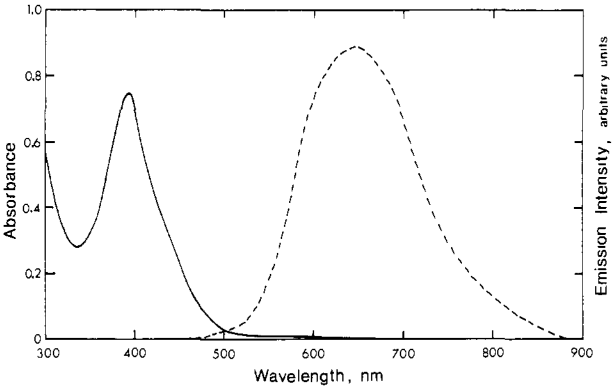

Figure 1. Electronic absorption (—) and emission (---) spectra of 10^{-4} M $Mo(CO)_5(4\text{-BNpyr})$ in benzene at 298 K. The emission spectrum is corrected for variations in instrumental response as a function of wavelength, and the excitation wavelength is 436 nm.

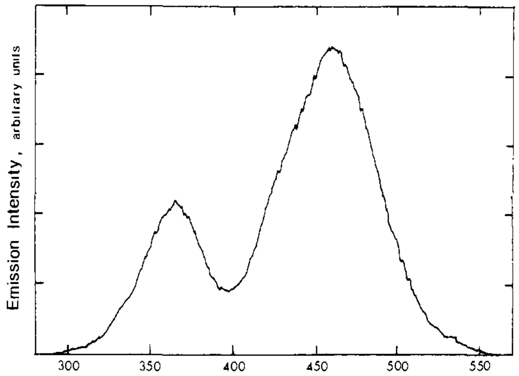

Figure 2. Excitation spectrum of 10^{-4} M $Mo(CO)_5(4\text{-BNpyr})$ in benzene at 298 K (emission monitored at 640 nm).

$Mo(CO)_5L$ complexes, where L is 4-ACpyr (4-acetylpyridine), 4-BNpyr (4-benzoylpyridine), 4-CNpyr (4-cyanopyridine), and 4-FMpyr (4-formylpyridine), were prepared via the tetrahydrofuran complex $Mo(CO)_5(THF)$ according to a procedure described previously.[5,10] The main impurities present, unreacted $Mo(CO)_6$ and L, were removed by column chromatography on alumina, followed by recrystallization from isooctane/benzene solution. Emitting or quenching impurities in the solvents (spectroscopic grade) were removed by several distillations. Carbonyl-containing impurities in the solvents were removed according to a literature procedure.[11]

The electronic absorption spectra recorded from filtered[12] solutions of $Mo(CO)_5(4\text{-ACpyr})$, $Mo(CO)_5(4\text{-BNpyr})$, Mo-

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[12] The $Mo(CO)_5L$ solutions were stringently filtered (at least twice through 0.22-μm millipore filters) to avoid the effects of particulate matter in the absorption and emission experiments.

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$(CO)_5$(4-CNpyr), and $Mo(CO)_5$(4-FMpyr) in benzene at room temperature are summarized in Table I. The electronic absorption spectrum obtained from a 10^{-4} M solution of $Mo(CO)_5$(4-BNpyr) in benzene is shown in Figure 1. Preliminary results have indicated that for each complex, the band maximum at 392–394 nm is relatively unaffected by changes in solvent, whereas the shoulder in the 430–450-nm region is affected both in intensity and position by the nature of the solvent.

The emission and excitation spectra recorded from deaerated,[13] filtered[12] solutions of $Mo(CO)_5$(4-ACpyr), $Mo(CO)_5$(4-BNpyr), $Mo(CO)_5$(4-CNpyr), and $Mo(CO)_5$(4-FMpyr) in benzene at room temperature were corrected for variation in instrumental response as a function of wavelength. The emission spectrum of 10^{-4} M $Mo(CO)_5$(4-BNpyr) in benzene is shown in Figure 1; the emission spectra obtained from the other complexes were similarly broad and unstructured and their maxima are listed in Table I. The spectral distribution of the emission was observed to be insensitive to excitation wavelengths longer than 280 nm for each complex. Emission quantum yields were calculated for the $Mo(CO)_5L$ complexes in benzene at room temperature by using a known emitter, $Ru(bpy)_3^{2+}$,[14] and the results are shown in Table I. The excitation spectrum of 10^{-4} M $Mo(CO)_5$(4-BNpyr) in benzene is shown in Figure 2 and shows features typical of those recorded from the $Mo(CO)_5L$ series. Two distinct bands are observed, centered at 366 and 455 nm. Corresponding features were recorded in the excitation spectra of $Mo(CO)_5$(4-ACpyr) at 375 and 431 nm, of $Mo(CO)_5$(4-CNpyr) at 343 and 469 nm, and of $Mo(CO)_5$(4-FMpyr) at 358 and 470 nm, all complexes being 10^{-4} M in benzene.

Although the synthesis of several $Mo(CO)_5L$ complexes has been reported,[1,2] this appears to be the first report for the $Mo(CO)_5$(4-substituted pyridine) series. The pyridine derivatives of metal carbonyls can be expected to exhibit low-energy MLCT excited states due to the low oxidation states of the metal. Thus, we assign the solvent-dependent long-wavelength shoulder (430–450-nm region) in the absorption spectra of the $Mo(CO)_5L$ complexes to be a MLCT transition. By comparing the absorption spectra of $Mo(CO)_5$(pyr) and $Mo(CO)_5$(pip) with the $Mo(CO)_5L$ complexes,[15] it is found that the strongly electron-withdrawing substituents yield substantially lower energy MLCT absorptions. Large substituent and solvent effects on the energy of the MLCT transition have been observed in the electronic absorption spectra of isoelectronic $W(CO)_5L$[3b,5b] and $Ru(NH_3)_5L^{2+}$[16] complexes. The absorption band at 392–394 nm for the $Mo(CO)_5L$ complexes is relatively insensitive to changes in the nature of ligand substituent and solvent medium. These absorptions are assigned to be due to a ligand field (LF) transition, in agreement with those reported for related carbonyl complexes.[2-5] The use of spin multiplicity designations has been avoided in these assignments because there is expected to be substantial coupling of spin and orbit angular momenta for the $Mo(CO)_5L$ complexes. Studies are in progress to gain further information about the character of the excited studies of $Mo(CO)_5L$ by using band analysis and MCD spectroscopy. Recent MCD analyses of the electronic excited states of $M(CO)_5L$ complexes, where M = Cr, Mo, or W and L = N or P donor, have appeared in the literature.[17,18]

Broad, unstructured emission with quantum yields of the order of 10^{-4}–10^{-3} was observed from the $Mo(CO)_5L$ complexes following excitation in room-temperature solution. A particularly novel aspect of these $Mo(CO)_5L$ complexes is that they appear to represent the first class of second-row transition-metal carbonyls known to luminesce in fluid solution. For these complexes the coupling of spin and orbital angular momenta is expected to be considerably less than the corresponding $W(CO)_5L$ series.[19] Due to the relative positions of the bands in the absorption and emission spectra of the $Mo(CO)_5L$ complexes, the emission is assigned to be from the low-lying MLCT excited state and is estimated to be at $(19.2 \pm 0.5) \times 10^3$ cm^{-1} for each complex. Importantly, for $Mo(CO)_5$(pyr), in which the lowest excited state is a LF one,[9] we were unable to observe emission in room-temperature solution.

The excitation and absorption spectra of $Mo(CO)_5$(4-BNpyr) under identical conditions are not congruent, indicating a wavelength dependence for ϕ_e. The most intense band at 455 nm is assigned to the MLCT emitting state. The excitation spectrum shows a minimum at 398 nm, close to that of the LF absorption. This result implies that the LF excited state does not efficiently populate the emitting state but that its energy degradation is by an alternative route. The LF excited state may be a reactive one; it has been attributed to be reactive for $W(CO)_5L$,[3b] $W(CO)_4L_2$,[3d] and $Ru(NH_3)_5L^{2+}$,[16a] complexes. The excitation band at 366 nm suggests the presence of an excited state, lying above the LF one, which can effectively populate the emitting state.

The lack of available data for the radiative and nonradiative processes has, up to the present time, inhibited models for the excited states of the group 6B metal carbonyls and their derivatives. We hope through temperature, solvent, and quenching studies to obtain detailed knowledge about the excited states of $Mo(CO)_5L$ and related complexes and to explore the possibility of excited-state tuning.[16b,20]

Acknowledgment. We are grateful to Professor Leslie M. Loew for use of the spectrofluorimeter and to Mary Bridge for technical assistance.

Registry No. $Mo(CO)_5$(4-ACpyr), 80925-81-1; $Mo(CO)_5$(4-BNpyr), 80925-82-2; $Mo(CO)_5$(4-CNpyr), 80925-83-3; $Mo(CO)_5$(4-FMpyr), 80925-84-4.

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Karachine: An Unusual Protoberberine Alkaloid

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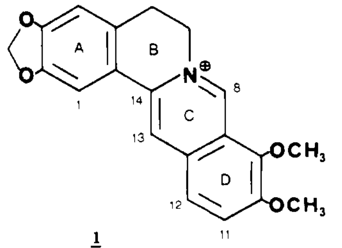
We describe the isolation and characterization of karachine (**2**),



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the first naturally occurring berbinoid incorporating acetone units and undoubtedly the most complex of the more than 50 protoberberine alkaloids presently known.

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