Emission of Tetracarbonylbis(pyridino)-Tungsten(0) and Related Complexes in Room Temperature Solution*

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Group 6B metal carbonyl complexes of the general formulae, $M(CO)_5L$ and $M(CO)_4L_2$, where M = Mo, W, and L = n-electron donor, have been reported to emit in a rigid environment, either in methylcyclohexane or EPA glasses at 77 K [2], or in methane and argon matrices at 12 K [3]. The lack of literature data concerning emission of Group 6B metal carbonyls in fluid solution has been attributed to the relatively efficient non-radiative pathways of the excited states of these complexes. Recently several complexes of the general formula, $M(CO)_5L$, where M = Mo, W, and L = 4-substituted pyridine, have been observed to luminesce under fluid conditions [4]. In each case the emission was shown to originate from a low-lying metal to ligand charge-transfer (MLCT) excited state. We are reporting here electronic absorption and emission data for a series of *cis*-$W(CO)_4L_2$ complexes in room temperature solution. This appears to represent the first class of $M(CO)_4L_2$ complexes known to be emissive under fluid conditions.

Experimental

The *cis*-$W(CO)_4L_2$ complexes, where L = py(pyridine), 4-Me-py (4-methylpyridine), 4-Et-py (4-ethylpyridine), 4-Ph-py (4-phenylpyridine), and 3,5-Cl_2-py (3,5-dichloropyridine), were prepared by irradiation of $W(CO)_6$ in N_2 purged hexane containing excess L [2e]. Purification was achieved by washing the product several times with hexane. Analyses (C, H, N) were satisfactory for all compounds. Spectroscopic grade benzene was distilled several times to ensure removal of emitting or quenching impurities. Carbonyl-containing impurities in the solvents were removed according to a literature method [5].

Results and Discussion

The electronic absorption spectrum of *cis*-$W(CO)_4(py)_2$ in benzene is shown in Fig. 1a. These absorption features have been assigned to be due to overlapping ligand-field (LF) and metal to ligand charge-transfer (MLCT) transitions [2e]. The electronic absorption spectral data for all the *cis*-$W(CO)_4L_2$ complexes studied are shown in Table I. The results show that as the electron withdrawing character of L is increased the MLCT shifts to lower energies and the LF absorption remains relatively unaffected in a manner previously reported for $W(CO)_5L$ complexes [2e, 4c]. In the electronic absorption spec-

TABLE I. Electronic Absorption and Emission Spectral Features for *cis*-$W(CO)_4L_2$ Complexes in Benzene at 298 K.[a]

L	Absorption	Emission[b]		
	Max. (λ, nm; (ε), M^{-1} cm^{-1})	Max. (nm)	Half-Width[c] (cm^{-1} × 10^3)	Quantum[d] Yield (×10^{-4})
4-Et-py	359(6650), 406(7320), ~455(sh)	565	5.7	0.5
4-Me-py	358(6760), 406(7390), ~455(sh)	575	6.0	0.3
py	367(6340), 412(7580), ~460(sh)	629	5.1	1.4
4-Ph-py	~382(sh), 434(8580), ~475(sh)	641	6.5	56.4
3,5-Cl_2-py	~382(sh), 438(7920), ~492(sh)	678	3.5	0.9

[a] $8 \times 10^{-5} - 2 \times 10^{-4}$ M deaerated solutions. [b] Emission spectra were corrected for variation in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [c] Width of emission band at half-height. [d] Measured relative to the emission of $Ru(bpy)_3^{2+}$ (ref. 10). Accurate to within ±15%.

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*See Ref. 1.

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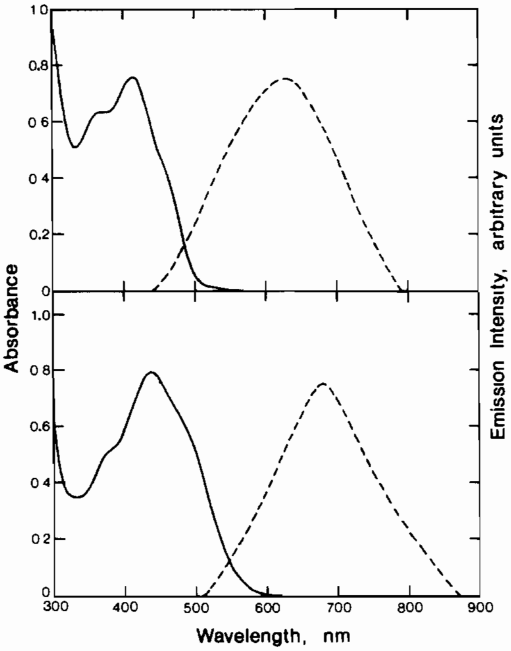

Fig. 1. Electronic absorption (———) and emission (------) spectra of a) *cis*-W(CO)$_4$(py)$_2$ and b) *cis*-W(CO)$_4$(3,5-Cl$_2$-py)$_2$ at equal concentration in benzene at 298 K. The emission spectra are corrected for variations in instrumental response as a function of wavelength and the excitation wavelength is 400 nm. Emission intensities are scaled arbitrarily to make maxima equal.

trum of *cis*-W(CO)$_4$(3,5-Cl$_2$-py)$_2$ in benzene (our extreme case) the MLCT absorption is at substantially lower energy (see Table I and Fig. 1b). In the absorption spectrum of *cis*-W(CO)$_4$(3,5-Cl$_2$-py)$_2$ in tetrahydrofuran the corresponding features were observed at 372 nm(sh), 425 nm and 476 nm(sh). This observation appears to be a general one for the *cis*-W(CO)$_4$L$_2$ complexes; in more polar media the MLCT transition shifts to higher energies [2e]. Similarly large solvent and substituent effects on the energy of the MLCT transition have been observed in the electronic absorption spectra of isoelectronic Mo(CO)$_5$L [4a], W(CO)$_5$L [2d, 4c], Ru(NH$_3$)$_5$L^{2+} [6] and Fe(CN)$_5$-L^{3-} [7] complexes.

The emission spectra of deaerated*, filtered** solutions of *cis*-W(CO)$_4$(py)$_2$ and *cis*-W(CO)$_4$(3,5-Cl$_2$-py)$_2$ in room temperature benzene are shown in Fig. 1. The emission spectra obtained from all the *cis*-W(CO)$_4$L$_2$ complexes studied at room temperature were similarly broad and unstructured and their data are summarized in Table I. The spectral distribution of the emission of each complex was observed to be independent of excitation wavelengths longer than 300 nm; this is consistent with emission from a single low-lying excited state. The emission data for the *cis*-W(CO)$_4$L$_2$ series show that as L becomes more electron withdrawing the emission maxima shift to lower energies. This effect is most pronounced for *cis*-W(CO)$_4$(3,5-Cl$_2$-py)$_2$ in which the emission is clearly attributable to the low-energy MLCT absorption (see Fig. 1b). We conclude that the emitting state of the *cis*-W(CO)$_4$L$_2$ complexes is MLCT in character.

Emission quantum yields (ϕ_e) have been measured for the *cis*-W(CO)$_4$L$_2$ complexes in benzene at room temperature using a known emitter, Ru(bpy)$_3^{2+}$ [8], and the results are shown in Table I. We note that ϕ_e varies by approximately two orders of magnitude, and attribute this to be a result of competition between the radiative and the non-radiative rate processes of these complexes. Interestingly, *cis*-W(CO)$_4$(4-Ph-py)$_2$ (our strongest emitter) has been reported to have a much reduced photoreactivity efficiency in a series of *cis*-W(CO)$_4$L$_2$ complexes [2d].

The emitting state of *cis*-W(CO)$_4$L$_2$ has been shown to be very sensitive to the nature of ligand and solvent. Through temperature and solvent studies of emission and photochemistry we hope to investigate excited state tuning effects [6e, 9] and obtain further information about the delicate photophysics of these complexes.

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*The *cis*-W(CO)$_4$L$_2$ solutions were purged with Ar for 20 mins prior to taking measurements to avoid oxygen quenching effects.

**The solutions were filtered through 0.22 μm millipore filters to avoid the effects of particulate matter in the absorption and emission experiments.

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