Emission and Photochemistry of the Lowest-Energy Excited States of Binuclear Group 6B Metal Carbonyl Complexes

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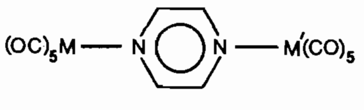
Recently several classes of mononuclear group 6B metal carbonyl complexes have been reported to emit in room temperature solution [1]. For each complex the emission was assigned to originate from a low-lying metal to ligand charge-transfer (MLCT) excited state. Binuclear complexes of the form $(OC)_5MpyrM(CO)_5$, where M = Cr, Mo, W, and pyr = pyrazine, are of considerable interest in this respect as their lowest-energy excited states are clearly MLCT, due to the low-lying π^*-acceptor orbitals of the pyrazine ligand [2–4]. The MLCT states of these binuclear complexes are so well separated from the higher-energy states that their photochemical properties can be studied exclusively. Furthermore, the mixed metal complexes of the form $(OC)_5MpyrM'(CO)_5$ (M,M′ = Cr, Mo, W) offer an opportunity to study the effects of different metals within the molecule on the low-lying excited states. To our knowledge the photophysical and photochemical properties of a binuclear metal carbonyl complex that is bridged through a coordinating ligand have not previously been investigated.



M,M′= Cr, Mo, W

The binuclear complexes were synthesized by thermally reacting photochemically generated $M(CO)_5THF$ with $M'(CO)_5pyr$ [5] according to a literature procedure [2]. We carried out this reaction in hexane (containing 0.1 *M* THF) rather than THF to avoid thermal decomposition of the products. This appears to be the first report of the synthesis of the mixed metal complexes. An alternative photochemical procedure was found to yield the $(OC)_5MpyrM'(CO)_5$ complexes, where M = M′. The initial photoproducts immediately combine to form $(OC)_5MpyrM(CO)_5$ which precipitates out of solution.

$$2M(CO)_6 \xrightarrow[\substack{\text{pyr}\\ \text{Ar purged}\\ \text{n-hexane}}]{h\nu,\ \lambda = 313\text{ nm}} M(CO)_5pyr +$$

$$+\ M(CO)_5(+2CO) \xrightarrow{\Delta} (OC)_5MpyrM(CO)_5$$

The products were purified by repeated washings with n-hexane followed by column chromatography on alumina. Analyses (C, H, N) were satisfactory for all compounds.

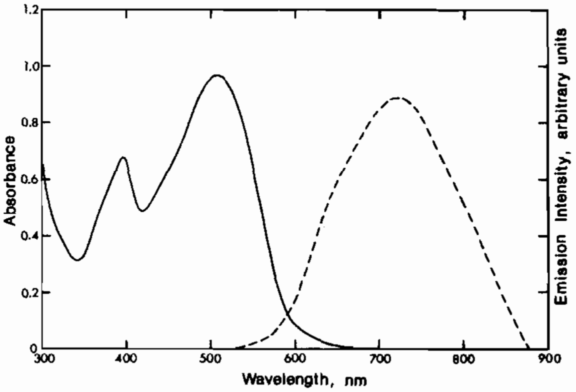


Fig. 1. Electronic Absorption (——) and emission (– – –) spectra of 8×10^{-5} *M* $(OC)_5WpyrW(CO)_5$ in benzene at 298 K. The emission spectrum is corrected for variation in instrumental response as a function of wavelength, and the excitation wavelength is 400 nm.

The electronic absorption and emission spectra for $(OC)_5WpyrW(CO)_5$ in benzene are shown in Fig. 1. Absorption and emission data for all the binuclear complexes studied are summarized in Table I. Each complex exhibits a characteristic absorption in the 385–410 nm region that is assigned to a ligand-field (LF) $^1A_1(e^4b_2^2) \rightarrow {}^1E(e^3b_2^2a_1^1)$ transition. This transition is at approximately the same position in the absorption spectra of the corresponding $M(CO)_5pyr$ species [6, 7] indicating that the local symmetry of the $M(CO)_5$ groups in $(OC)_5MpyrM'(CO)_5$ is preserved. The LF transition is characteristically not solvent dependent [1]. In contrast the low-energy absorption in the 480–520 nm region is substantially red-shifted in iso-octane and is assigned to a $M \rightarrow \pi^*$ (pyr) charge-transfer transition [2–4]. It is noted that the low-energy absorptions of the tungsten complexes in iso-octane each show the presence of two $M \rightarrow \pi^*$(pyr) transitions. Similarly resolved features have also been observed for these complexes in tetrachloroethylene and carbon tetrachloride. Recently Daamen *et al.* have obtained evidence for y and z polarized MLCT transitions in $(OC)_5WpyrW(CO)_5$ using resonance Raman spectroscopy [3]. For any

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TABLE I. Electronic Absorption and Emission Spectral Features for $(OC)_5MpyrM'(CO)_5$ Complexes in Benzene (Iso-octane)[a].

Complex M, M′	Absorption[b] Max. (nm)	Emission[c,d] Max (nm)	Half-Width ($cm^{-1} \times 10^{-3}$)	Quantum Yield ($\times 10^{-4}$)
Cr, Cr	408(408), 516(572)	702	3.7	0.6
Cr, Mo	395(400), 504(562)	687	3.9	1.4
Mo, Mo	388(388), 484(536)	675	3.8	3.9
Mo, W	392(392), 498(544, 573)	712	2.9	4.6
W, W	397(397), 510(552, 595)	722	3.5	5.0
W, Cr	399(399), 514(548[e], 586)	707	3.5	1.5

[a] 8×10^{-5}–2×10^{-4} deoxygenated solutions. [b] Recorded at 298 K. [c] Recorded at 283 K except for M,M′ = W, W. [d] Emission spectra were corrected for variation in instrumental response as a function of wavelength. The excitation wavelength is 400 nm. [e] Observed as a shoulder.

particular solvent the energies of the M → π*(pyr) absorptions are ordered Mo > W > Cr [2] consistent with that reported for series of mononuclear carbonyls [8]. The M → π*(pyr) absorptions of the complexes where M ≠ M′ are at energies between those of the respective M = M′ complexes.

Each complex exhibited broad, unstructured emission in the 550–850 nm region; the energies of the emission maxima closely parallel those observed in absorption (see Table I). The emission is assigned to the lowest-lying M → π* excited state for each complex, analogous to the MLCT emission observed from $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ complexes, where L = a substituted pyridine [1]. These $(OC)_5MpyrM'(CO)_5$ species represent the first binuclear group 6B metal carbonyl complexes known to emit in fluid solution. Emission spectra were recorded at 283 K for several of the complexes to avoid thermal substitution reaction. Attempts to obtain emission data in iso-octane were unsuccessful due to the low solubility of the complexes. Emission quantum yields were calculated for the binuclear complexes by using a known emitter, $Ru(bipy)_3^{2+}$ [9].

Irradiation into the low-energy W → π*(pyr) absorption of $(OC)_5WpyrW(CO)_5$ breaks the W–N bond. In the presence of excess entering ligand the reaction proceeds cleanly to form mononuclear products with an isosbestic point at 418 nm (see Fig. 2).

$$(OC)_5WpyrW(CO)_5 \xrightarrow[pyr]{h\nu,\ \lambda = 514\ nm} 2W(CO)_5pyr$$

The photochemical efficiency of this reaction is low, quantum yield = 0.0013 at 293 K; this is also a characteristic of $W(CO)_5L$ complexes that emit in room temperature solution [1b]. The thermal decomposition of $(OC)_5MopyrMo(CO)_5$ in the presence of excess pyrazine has also been reported to proceed by the above route [4].

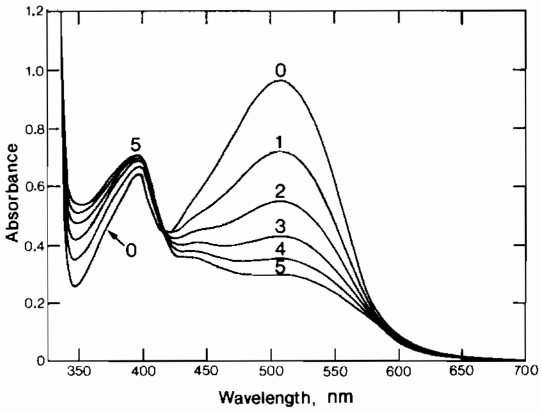

Fig. 2. Electronic absorption spectral changes accompanying the 514.5 nm irradiation (equal time intervals) at 293 K of 7.8×10^{-5} *M* $(OC)_5WpyrW(CO)_5$ in benzene containing 0.1 *M* pyrazine.

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