

Ligand Field Luminescence of $[\text{ClRe}(\text{CO})_4\text{L}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}]$ ($\text{L} = \text{NH}_3, \text{NC}_5\text{H}_{11}, \text{PPh}_3$) Complexes in Room-temperature Solution

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Room-temperature ligand field luminescence has been observed from $[\text{ClRe}(\text{CO})_4(\text{pip})]$, $[\text{ClRe}(\text{CO})_4(\text{PPh}_3)]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NH}_3)]$, and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$ (pip = piperidine) complexes.

Luminescence techniques have proven to be very useful as spectroscopic probes for the determination of photophysical processes in transition-metal complexes.¹ In particular, complexes which luminesce in fluid solution yield valuable photophysical rate data under conditions where photochemistry normally takes place.^{2,3} However, unlike classical co-ordination compounds, there are relatively few classes of organometallic complexes that have been established to luminesce in fluid solution, and these have been limited to systems which exhibit lowest-lying intraligand (I.L.) or charge-transfer (C.T.) excited states.³ This paper reports absorption, emission, and excitation spectral data obtained from two classes of rhenium carbonyls in room-temperature solution; for each complex the emission arises from a lowest-lying ligand field (L.F.) state. These results demonstrate that luminescence studies in solution may be informative for the vast array of transition-metal organometallic complexes which exhibit lowest-lying L.F. excited states, despite the high photoreactivities typically associated with these systems.

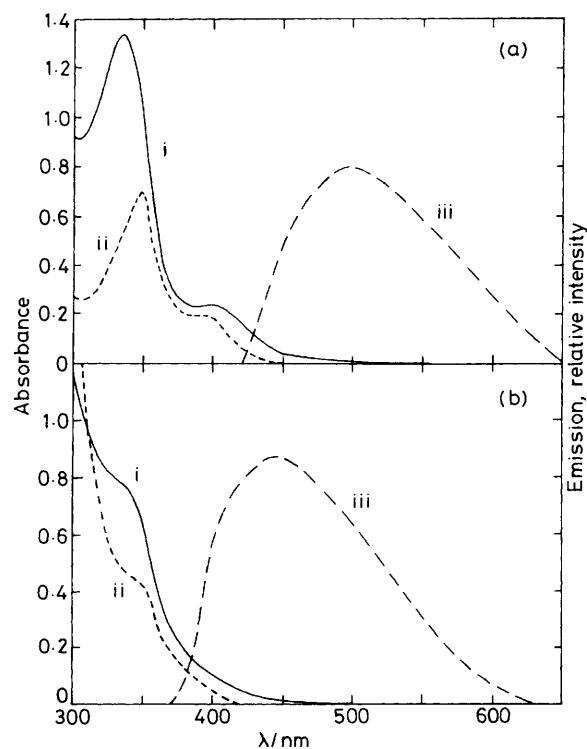


Figure 1. Electronic absorption (i), excitation (ii), and emission spectra (iii) of (a) $[\text{ClRe}(\text{CO})_4(\text{pip})]$ and (b) $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$ in deaerated benzene at 293 K. Excitation and emission spectra are corrected for instrumental response as a function of wavelength. Excitation spectra were recorded with emission monitored at its maximum. Emission spectra were recorded following excitation at 330 nm.

Complexes $[\text{ClRe}(\text{CO})_4(\text{pip})]$, $[\text{ClRe}(\text{CO})_4(\text{PPh}_3)]$, $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NH}_3)]$, and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$ (pip = piperidine) were prepared from the parent $[\text{ClRe}(\text{CO})_5]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ compounds according to published procedures.⁴⁻⁶ These complexes were isolated as solids, redissolved in cyclohexane, and purified by recrystallization under a dry N_2 atmosphere. In some cases sublimation techniques were required to remove unchanged starting materials. I.r. and u.v.-visible spectra obtained for the product complexes were in agreement with literature values.⁴⁻⁶

Electronic absorption, emission, and excitation spectra determined for $[\text{ClRe}(\text{CO})_4(\text{pip})]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$ complexes in deaerated benzene at 293 K are shown in Figure 1. Emission and excitation spectra were recorded on an SLM Instruments Model 8000/8000S spectrometer which incorporates photon counting facilities. Emission lifetimes were recorded on a PRA System 3000 single-photon counting lifetime apparatus. The relevant data obtained from all of the complexes are summarized in Table 1. The emission spectral distribution of each complex was observed to be independent of excitation wavelength in the 300–350 nm region indicating that the emission apparently arises from a single excited state. Moreover, the congruent spectral features of the absorption and excitation spectra (see Figure 1) indicate that the luminescence occurs from the lowest energy excited state in each of these complexes. Importantly, luminescence was not detected from the parent $[\text{ClRe}(\text{CO})_5]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ compounds, or from the free ligands, under experimental conditions identical to those used in obtaining spectra from the substituted complexes.

Previously, the lowest-lying excited states in $[\text{ClRe}(\text{CO})_4\text{L}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}]$ ($\text{L} = \text{CO}$, P-donor, and N-donor ligand) complexes have been assigned to be of metal to ligand charge-transfer (M.L.C.T.) or ligand field (L.F.) characters,

Table 1. Electronic absorption, excitation, and emission spectral data for $[\text{ClRe}(\text{CO})_4\text{L}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{L}]$ complexes in deaerated benzene at 293 K.

Complex	Absorption $\lambda_{\text{max}}/\text{nm}$	Excitation ^a $\lambda_{\text{max}}/\text{nm}$	Emission ^b		
			$\lambda_{\text{max}}/\text{nm}$	$\phi^c \times 10^2$	τ/ns
$[\text{ClRe}(\text{CO})_4(\text{pip})]$	336,402	352,398	498	1.64	2.0
$[\text{ClRe}(\text{CO})_4(\text{PPh}_3)]$	336,369	334,355	402	0.27	1.2
$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NH}_3)]$	338	348	424	0.08	^d
$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$	338	344	440	0.13	0.5

^a Corrected excitation spectra with emission monitored at the emission maximum. ^b Corrected emission spectra; excitation wavelength is 330 nm. ^c Measured relative to value of 0.55 reported for quinine sulphate in 0.2 M H_2SO_4 (see ref. 7). ^d Value unobtainable owing to thermal decomposition of the complex.

depending on the nature of the ligand L. In the absence of a low-lying π^* -acceptor orbital (as in these NH_3 , pip, and PPh_3 derivatives) the L.F. excited state is attributed to be at lowest energy.^{4,6} The electronic absorption data of Table 1 are in accordance with this assignment, following the order $\text{CO} > \text{P-donor} > \text{N-donor}$ in L.F. strength. Therefore, the emission and excitation results obtained here are consistent with radiative decay from the lowest-lying L.F. states in each of these complexes. Emission measurements in 5 : 5 : 2 v/v ether: isopentane: ethanol (EPA) glasses at 80 K further support a L.F. assignment: $[\text{ClRe}(\text{CO})_4(\text{pip})]$ emits at λ_{max} 460 nm and $\tau = 8.9 \mu\text{s}$; $[\text{ClRe}(\text{CO})_4(\text{PPh}_3)]$ emits at λ_{max} 394 nm and $\tau = 5.3 \mu\text{s}$; $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{NH}_3)]$ emits at λ_{max} 416 nm and $\tau = 6.6 \mu\text{s}$; and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2(\text{pip})]$ emits at λ_{max} 432 nm and $\tau = 11.5 \mu\text{s}$.

Although L.F. states are believed to be lowest-lying for the parent $[\text{ClRe}(\text{CO})_5]$ molecule,⁶ the absence of room-temperature emission suggests that these energy levels may be heavily mixed with states of other orbital character, or that their radiative processes may be internally quenched by other close-lying excited states. Previously it has been reported that the lowest energy ${}^1\text{A}_1(\text{e}^4\text{b}_2^2) \rightarrow {}^1\text{E}(\text{e}^3\text{b}_2^2\text{a}_1^1)$ L.F. states in $[\text{ClRe}(\text{CO})_5]$ contain substantial $\text{Cl}(\pi) \rightarrow (\text{d}\pi)\text{M}$ C.T. character.^{6,8} Furthermore, in $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_3]$ it has not been conclusively established that the L.F. transition is lowest lying and $\text{M}(\text{d}\pi) \rightarrow (\pi^*)\text{CO}$ and $\text{M}(\text{d}\pi) \rightarrow \pi^*(\text{C}_5\text{H}_5)$ states are thought to be close in energy.^{9,10}

Photophysical events from L.F. states of organometallic compounds have typically been characterized by rapid bond dissociation and efficient photoreactivity.¹⁰ Therefore, although L.F. luminescence is commonly observed from organometallic complexes in a rigid glass or matrix environment where photodissociation pathways are inefficient, these observations of room-temperature solution L.F. emissions are unusual. The emission lifetimes determined in this work are

short, but this is not unexpected for excited states that deactivate rapidly *via* nonradiative processes. Further luminescence studies are in progress to probe the excited states processes of a wide range of organometallic molecules that exhibit low-lying L.F. states.

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