Photoluminescence From Copper(I) Complexes With Low-lying Metal-to-Ligand Charge Transfer Excited States

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Summary Exciting the metal-to-ligand charge transfer excited states of several Cu^I complexes gives rise to photoluminescence which appears to originate from the charge transfer excited states.

Photostudies of complexes with low-lying metal-to-ligand charge transfer (MLCT) excited states have been of considerable interest recently. The majority of the work has involved d^6 ions,[1] although d^8 systems have also been studied.[2] Photoluminescence and photochemistry have been observed from such states, the dominant type of photochemistry being photoredox chemistry.[3] We have begun studies of d^{10} systems with low-lying MLCT states, especially Cu^I systems,[4,5] and we now report that many of these exhibit emission which appears to involve the charge transfer excited states. The present results support the idea[4,5] that relatively long-lived photoexcited Cu^I systems can survive to take part in bimolecular reactions, and point to the possibility of carrying out parallel studies of the photochemistry and the photoluminescence of these systems.

We have studied complexes involving ligands with low-lying, unoccupied π^* levels such as 2,9-dimethyl-1,10-phenanthroline (dmp). Spectral data for three representative systems are in the Table. In each case a strong MLCT transition is observed in the visible or near-u.v.

TABLE. Spectral data of selected Cu^I complexes

Complex	Absorption[a] maximum/nm	ϵ/l mol^{-1} cm^{-1}	Emission[b] maximum/ nm	Emission[b] lifetime/ ns
$[Cu(PPh_3)_2(bpy)]^{+}$[c]	356	3640	610	<1
$[Cu(dpe)(bpy)]^{+}$[d]	398	2890	612	<1
$[Cu(dmp)_2]^{+}$	454	8430	710	—

[a] Obtained in ethanol at room temperature. [b] Obtained in alcohol at 77 K. [c] bpy= 2,2′-bipyridine. [d] dpe=*cis*-Bis(1,2-diphenylphosphino)ethylene.

In all cases photoluminescence is observed in an ethanol glass at 77 K and in each case it is considerably red-shifted from the corresponding MLCT absorption band. The absorption and emission bands are rather broad and unstructured, except in the case of $[Cu(dmp)_2]^+$.

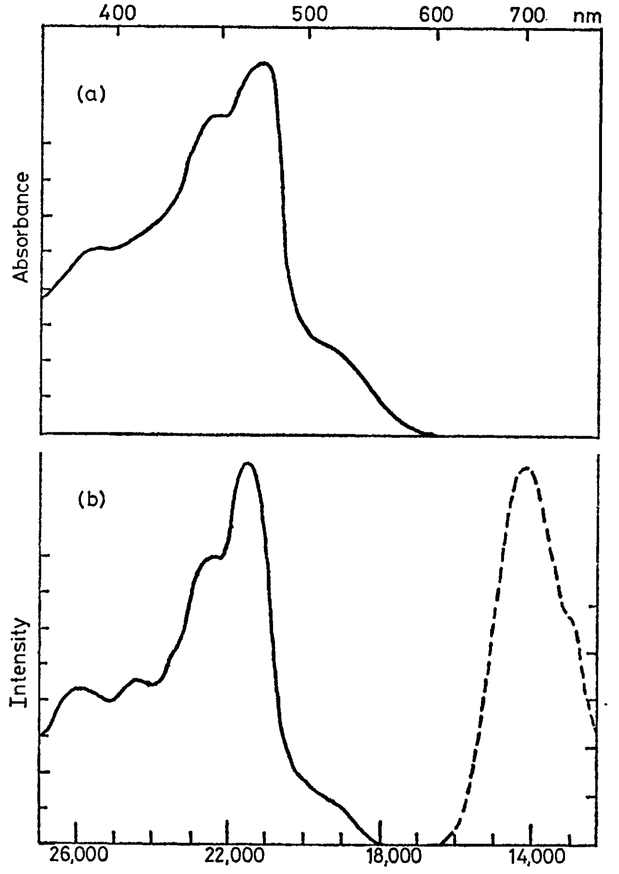

FIGURE 1. The spectra of $[Cu(dmp)_2]^+$ measured in an ethanol glass at 77 K: (a) absorption spectrum; (b) excitation spectrum (—) and emission spectrum (- - - -).

Figure 1a shows the visible absorption spectrum of $[Cu(dmp)_2]^+$ in ethanol at 77 K. In part, the structure in the spectrum reveals vibronic components associated with the main transition, which has previously been assigned MLCT character.[6] However, the complexity of the spectrum suggests that more than a single MLCT state is involved in this region of the spectrum. Figure 1b presents the photoluminescence spectrum of $[Cu(dmp)_2]^+$ and the corrected excitation spectrum. Figure 2 presents photoluminescence spectra of the PPh_3 and bpy ligands as well as that of the $[Cu(PPh_3)_2(bpy)]^+$ system.

A priori, one must consider that the emission could be ligand-centred, metal-centred, or charge transfer in character. For these systems at least, it appears unlikely that the emission could be a predominantly ligand-centred process, because previous studies have shown that ligand-centred emission from transition metal complexes is only slightly shifted in energy ($\leqslant$ 1000 cm^{-1}) from the emission of the unco-ordinated ligand.[1,7] As is evident in Figure 2, the emission we report is well shifted ($>$5000 cm^{-1}) from any ligand emission.

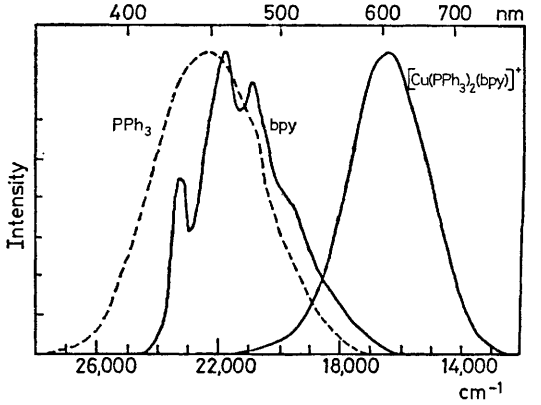

FIGURE 2. The photoluminescence spectra of PPh_3 (- - - -), bpy (—) in higher energy region, and $[Cu(PPh_3)_2(bpy)]^+$ (—) in lower energy region measured at 77 K in an ethanol glass.

The possibility that the emission could reflect a metal-centred process is more difficult to dismiss on energy grounds. Such emission ($3d^94s^1 \rightarrow 3d^{10}$) has been observed for some Cu^I systems,[8] and it is difficult to predict the energy at which this emission would be expected for a particular system. However, $3d^94s^1 \rightarrow 3d^{10}$ emission is orbitally forbidden† and has been observed to have a lifetime in the microsecond domain.[8] On the other hand, charge transfer emission should be orbitally allowed and could well exhibit a very short lifetime. It should also be noted that in all cases the reported emission spectra approximately mirror the corresponding MLCT bands of the complexes. All things considered, we think it is most reasonable to suppose

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† Symmetry considerations may relax this selection rule somewhat, but it is expected to apply to a first approximation at least for the case of a predominantly metal-centred emission.

that in each case the emission originates from a state which involves predominantly charge transfer character. Of course the emitting states could involve admixtures of states associated with ligand-centred and/or metal-centred excited configurations as well.

The sub-nanosecond lifetimes observed for the mixed ligand systems are sufficiently short to suggest that the emission originates from singlet levels. We were unable to measure a lifetime for the $[Cu(dmp)_2]^+$ system in an ethanol glass because the transient detection system available was very insensitive above *ca.* 650 nm. We should note, however, that the emission is easily seen by the eye at 77 K and can also be seen by the eye in solution at room temperature.

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