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Photochemical and photophysical properties of $[Mn(imidazole)(CO)_3(phen)](SO_3CF_3)$ complexes

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Abstract

The photoreactions resulting from metal-to-ligand charge transfer (MLCT) excitation of the manganese(I) tricarbonyl complexes *fac*-$[Mn(CO)_3(phen)(Im)](SO_3CF_3)$ and *fac*-$[Mn(CO)_3(phen)(Im\text{-}CH_3)](SO_3CF_3)$ in several solvents at various wavelengths are reported. In each case, the reaction product is the corresponding *mer*-$[Mn(CO)_3(phen)(Im\text{-}L)]^+$ isomer. The high quantum yields, ∼0.66 mol einstein^{-1}, reflect accurately primary photoprocesses from ligand-field states which are measured in a time scale during which thermal or secondary photoprocesses are not important. Further, in competition to ligand-field photoisomerization, these complexes are luminescent at room temperature. The emitting state can be tuned from a MLCT emission to intra-ligand (IL) fluorescence by varying the solvent polarity and excitation wavelength. Alterations in the character of the excited state result in large changes in the emission spectra suggesting the use of these complexes as probes. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Tricarbonyl-manganese(I) complexes; Photochemistry; Photophysics

1. Introduction

There has been considerable interest in the photophysics and photochemistry of transition-metal complexes that have low-lying metal to ligand charge-transfer (MLCT) excited states. For example, $[Ru(NH_3)_5(py\text{-}X)]^{2+}$ [1–4], where py-X is pyridine or a substituted pyridine; $Re(CO)_3(\alpha\text{-diimine})X$ [5–16], and $Mn(CO)_3(\alpha\text{-diimine})X$ [17–21], where X is halide, have been extensively studied. The results of these studies have shown that the luminescence and photochemical characteristics of the complexes are dependent on the positions of the low-lying MLCT excited-state. Small changes in the nature of the ligands (L) and (X) can have a major effect on the properties of the complex; therefore, the ligand substituent can be used to 'tune' the excited states and the photochemical properties of transition metal complexes [2–4,22].

In the case of Mn(I) complexes, a strikingly contrasting photochemical behavior has been observed when irradiating in its MLCT absorption bands [17–21]. In fluid solutions at room temperature, $[Mn(L)(CO)_3(\alpha\text{-diimine})]^{0/+}$ (L=π–, σ-donor) and $[Mn(L)(CO)_2(\eta^5\text{-}C_5H_5]^+$ (L=π-acceptor) complexes are both not luminescent, but while MLCT excitation of the former leads to homolysis of the Mn–CO bond producing dimers [17,20], irradiation of the latter ions results exclusively in L substitution [21].

In recent studies, we have been investigating the effect of the ligand field strength on the electronic absorption properties of Mn(I) complexes [23]. In these studies, it has been shown that replacement of the bromide ligand by a strong σ-donor ligand like imidazole, is an effective way of altering the energy states of *fac*-$[Mn(CO)_3(phen)L](SO_3CF_3)$. Thus, in the case of the imidazole complex, the lowest energy transitions will have MLCT character. It is known that the related *fac*-$[Re(CO)_3(phen)L](SO_3CF_3)$ complex emits in solution at 298 K [24]. Therefore, similar Mn(I) complexes can be expected to exhibit emission under conditions where only photochemistry was observed so far [17–21].

This paper describes the results of the photochemical and photophysical behavior of *fac*-$[Mn(CO)_3(phen)(Im\text{-}L]^+$ (L=–H or $–CH_3$) complexes. In addition to CO loss, MLCT excitation of these complexes in solution leads to luminescence at room temperature.

2. Experimental section

2.1. Materials

Analytical grade chemicals and HPLC grade solvents were used for all experiments. The manganese(I) compl-

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exes [Mn(CO)$_3$(phen)(Im)](SO$_3$CF$_3$) and [Mn(CO)$_3$(phen)(Im-CH$_3$)](SO$_3$CF$_3$) were prepared by the reaction of the triflate complexes [Mn(CO)$_3$(phen)(SO$_3$CF$_3$)](SO$_3$CF$_3$) with imidazole at room temperature according to the method described previously [23]. The solvents dichloromethane and tetrahydrofurane were dried with P_2O_5 and distilled under N_2 atmosphere before use. The chemical actinometer potassium (tris-oxalate) ferrate(III), was prepared according to Calvert and Pitts [25].

2.2. Instruments

Monochromatic irradiations at 334, 366 and 436 nm were carried out using a 200-W Xenon lamp in an Oriel mod. 68805 Universal Arc Lamp source selected with a monochromator. The progress of the photoreactions was monitored spectrophotometrically on an Hitachi model U-2000 spectrophotometer. Emission spectra were recorded with a F-4500 Hitachi spectrofluorometer.

2.3. Procedures

Photolysis experiments were carried out at 25°C in 1.0 cm pathlength quartz cells capped with a rubber septum. The solutions (10^{-4} M initial complex concentration) were deaerated by bubbling with argon prior to photolysis, and stirred during irradiation. The solutions were photolyzed up to 20% conversion. Simultaneous dark reactions were carried out with identical solutions. These samples were completely stable in the dark on a time scale longer than that of the photochemical experiments.

The quantum yields for disappearance of starting material were calculated from the decrease of the MLCT absorption band. The reported quantum yields are the average of, at least, three independent experiments.

3. Results

3.1. Electronic absorption spectra

The electronic absorption spectrum of *fac*-[Mn(CO)$_3$(phen)(Im-CH$_3$)] is shown in Fig. 1, and a similar spectrum is observed for the L=H complex. The spectra are characterized by two rather strong bands in the UV–VIS region around 400 and 240 nm. In a previous study [23], the lower energy band has been assigned to the MLCT transition to the lowest π^* orbital of phen. This attribution was based on the high intensity of the band, its solvatochromism, and the relatively sensitivity to substituents on the imidazole ligand. The higher energy band was assigned to the intra-ligand π–π^* transition.

3.2. Photochemistry

Irradiation of *fac*-[Mn(CO)$_3$(phen)Im-L]$^+$ (L=–H, –CH$_3$) in CH$_2$Cl$_2$ solution at 366 nm leads to the decrease of the characteristic absorption at ~376 nm (Fig. 2) and the appearance of a new band at ~600 nm. Isosbestic points were well preserved up to ~20% conversion, indicating that neither side reactions nor product photodecomposition occurs. The photoproducts were identified by comparing the IR and UV–VIS spectra with those of previously characterized similar or structurally closely related complexes [26–28]. The results collected in Table 1 clearly show that all quantum yields are very similar and do not show any systematic dependence on the excitation energy, complex concentration (1–5×10^{-4} M) or light intensity (0.2–1.0×10^{-9} einstein s^{-1}). The quantum yields measured for both compounds may be regarded as nearly identical, as well.

Contrary to the behavior of the related Mn(CO)$_3$(bpy)(Br) complex [17–21], the irradiation of *fac*-[Mn(CO)$_3$(phen)(Im-L)]$^+$ at the wavelength of its lowest energy MLCT band does not result in new absorption bands that could

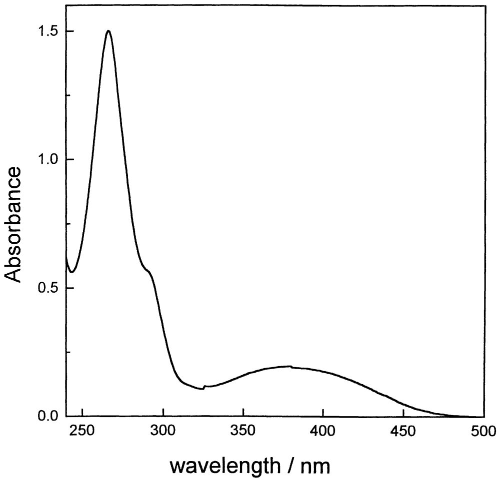

Fig. 1. Absorption spectrum of *fac*-[Mn(CO)$_3$(phen)(Im-CH$_3$)]$^+$ in CH$_2$Cl$_2$.

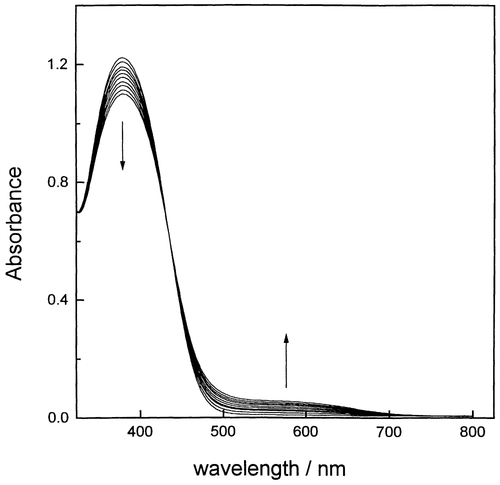

Fig. 2. Changes in the absorption spectrum resulting from 366 nm photolysis of *fac*-[Mn(phen)(CO)$_3$(Im-CH$_3$)]$^+$~10^{-4} M in CH$_2$Cl$_2$.

Table 1
Quantum yields Φ for the photolysis of *fac*-[Mn(phen)(CO)$_3$(Im-L)]$^+$ in various solvents at 25°C. [Complex] ca. 10^{-4} M

Solvent	L	λ_{max} (nm); ε (l mol^{-1} cm^{-1})	λ_{irr} (nm)	Φ (mol einstein^{-1})
CH_2Cl_2	–H	378(3700); 266(31,500)	334	0.70±0.02
			366	0.66±0.04
			436	0.60±0.03
	$–CH_3$	376(3700); 266(30,000)	334	0.70±0.02
			366	0.69±0.02
			436	0.62±0.02
THF	–H	371(4000); 266(31,000)	334	0.66±0.03
			366	0.64±0.02
			436	0.62±0.01
	$–CH_3$	376(3300); 266(29,000)	334	0.67±0.01
			366	0.64±0.03
			436	0.68±0.05
MeOH	–H	369(3200); 266(27,000)	334	0.60±0.01
			366	0.66±0.06
			436	0.69±0.04
	$–CH_3$	372(3000); 266(26,000)	334	0.70±0.04
			366	0.70±0.03
			436	0.68±0.02
CH_3CN	–H	370(3600); 267(26,000)	334	0.62±0.01
			366	0.64±0.03
			436	0.66±0.03
	$–CH_3$	372(3000); 266(25,000)	334	0.64±0.02
			366	0.70±0.04
			436	0.68±0.03

be assigned to the dimer [Mn$_2$(CO)$_6$(phen)$_2$], similar to those found for the dimer of the bipyridyl complex [Mn$_2$(CO)$_6$(bpy)$_2$] (bands at 840, 755(sh), 655, 466 nm, in THF solution [26,27]). No intermediate complex or free CO (2143 cm^{-1}) were detected in the ν(CO) region during irradiation at 366 nm of *fac*-[Mn(CO)$_3$(phen)(Im-L)]$^+$ monitored by IR spectroscopy. Furthermore, photolysis in the presence of an excess of phosphine (1/100) lead only to the formation of the *mer*-[Mn(CO)$_3$(phen)Im]$^+$ isomer, with a quantum yield (0.66 mol einstein^{-1}) identical to those obtained in the absence of phosphine. The isosbestic points in the spectra indicate that the reaction takes place without formation of side- or secondary photoproducts. In addition, the photolysis product absorbs around 500 nm ($\varepsilon \sim 10^3$ l mol^{-1} cm^{-1}, similar to *mer*-Mn(CO)$_3$(bpy)(Br) [28]. These results suggest a simple *fac*- to *mer*-photoisomerization as indicated in reaction 1, with the lowest energy ligand field state as the precursor.

$$fac\text{-}[\mathrm{Mn(CO)_3(phen)(Im\text{-}L)}]^+ \xrightarrow{h\nu} mer\text{-}[\mathrm{Mn(CO)_3(phen)(Im\text{-}L)}]^+ \quad (1)$$

3.3. Photophysics

Luminescence of Mn(I) complexes has never been reported before. Also, we have been unable to detect luminescence from the MnBr(CO)$_3$(phen) complex. By contrast, the *fac*-[Mn(CO)$_3$(phen)(Im-L)]$^+$ complexes exhibit luminescence after excitation at room temperature in fluid solutions.

Typical emission spectra of the complexes and free ligand phenanthroline in dichloromethane at room temperature are shown in Fig. 3. Spectra were recorded exciting at 255 nm, the absorption maximum of the free ligand (Fig. 3A), and the absorption maximum of the complex at 370 nm (Fig. 3B). The emission spectrum of the free ligand when excited at 255 nm consists of an intense and well structured band in the 350 nm region, corresponding to the $^1\pi$–π* transition. Under the same conditions, the Mn(I) complexes emit quite weakly.

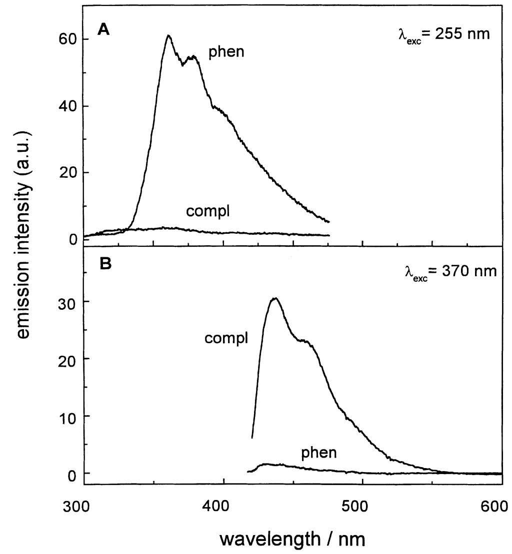

Fig. 3. Emission spectra of *fac*-[Mn(phen)(CO)$_3$(Im)]$^+$ and free phenanthroline: (A) excitation at 260 nm; (B) excitation at 370 nm. Conc. ca. 10^{-5} M in CH_2Cl_2.

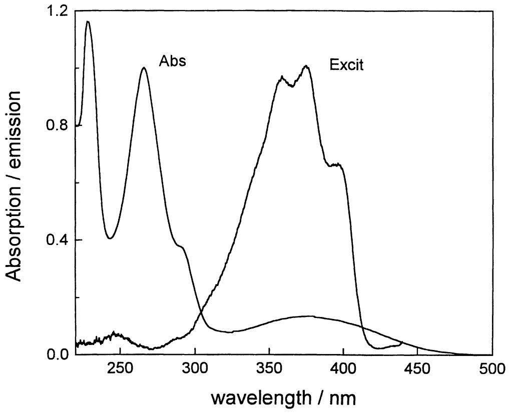

Fig. 4. Absorption and excitation (λ_{em}=460 nm) spectra of *fac*-[Mn(phen)(CO)$_3$ (Im)]$^+$ in CH_2Cl_2. Conc. ca. 10^{-5} M.

By contrast, when exciting the *fac*-[Mn(CO)$_3$(phen)(Im)]$^+$ complex at 370 nm the emission spectrum is characterized by a broad emission with a maximum at 435 nm and a shoulder at 470 nm. This emission is assigned to a MLCT transition, as expected from the absorption spectrum of the complex shown in Fig. 1. The singlet emission of phenanthroline coordinated in the complex at 350 nm is practically completely quenched possibly due to the enhancement of the intersystem conversion by the heavy atom effect of the metal ion. No phosphorescence emission from the phenanthroline $^3\pi\pi$ level is observed at room temperature. It can clearly be seen from the excitation spectrum in Fig. 4 that the emission originates basically from the absorption in the MLCT band, with little or none energy transfer from the ligand $\pi\pi$ system.

The energy of the MLCT state depends on the nature of the solvent and temperature. As can be seen comparing Figs. 3 and 5, the emission intensity of the complex excited at 370 nm is weaker and red-shifted in MeOH compared to dichloromethane, Fig. 5A.

On the other hand, when exciting *fac*-[Mn(phen)(CO)$_3$ (Im-L)]$^+$ at 260 at 77 K, an emission is observed in the 450–550 nm region, as shown in Fig. 5C. This emission appears in the same region and has structural features very similar to that of free phenanthroline in the same conditions, also shown for comparison. Therefore, the emission of the complex in this region has to be assigned to the radiative decay of the $\pi\pi$ triplet of state of the coordinated ligand, since the phenanthroline energy manifold is not significantly affected by the coordination of the ligand to the central metal ion, as can deduced comparing the absorption spectra in the 220–250 nm region.

When exciting the complex at 370 nm at low temperature, the emission is similar to that observed in MeOH at room temperature, although slightly red-shifted and weaker, but remains structureless. In these conditions, the ligand phenanthroline does not luminescence. A comparison of the shape and intensity of the emission bands of the complex excited at 370 nm and that of the free ligand excited at 260 nm, suggests that this band corresponds to the same MLCT transition observed at room temperature in MeOH or CH_2Cl_2.

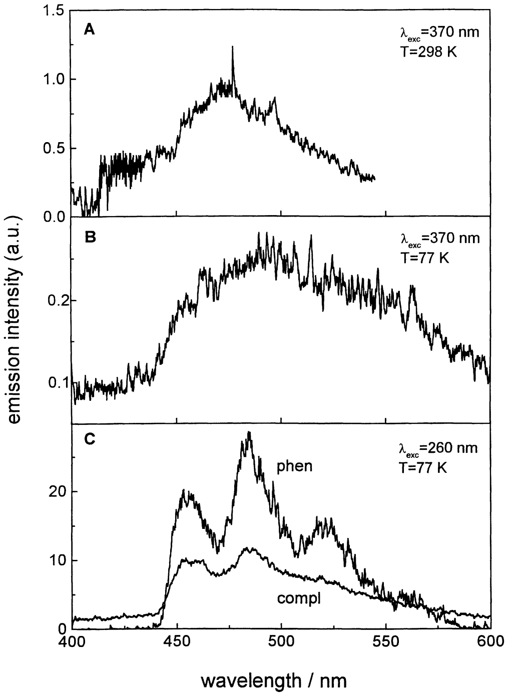

Fig. 5. Emission spectra in methanol of the complex at room temperature (A) and 77 K (B) excited at 370 nm; and of the complex and phenanthroline at 77 K, excited at 260 nm.

4. Discussion

4.1. Photochemistry

The *fac-mer* photoisomerization process is presumably coupled to ligand photolabilization, as has been demonstrated for many hexacoordinated d^6 complexes [29–32]. On one side, the lack of substantial dependence of the quantum yields with the coordinating ability of the solvents is consistent with a dissociative type mechanism for photosubstitution of CO. On the other hand, it is well known that thermal rearrangements of unsaturated transition metal carbonyls often occur, like the *cis*-labilization in Mn(CO)$_5$Br and Re(CO)$_5$Br in the CO dissociation [33], and others [34–38].

Photolysis of *fac*-[Mn(CO)$_3$(phen)(Im-L)]$^+$ under CO bubbling results in *mer*-[Mn(CO)$_3$(phen)(Im-L)]$^+$ formation with quantum yields 0.68 and 0.66 for L=–H and –CH$_3$, respectively, comparable to those for reaction 1 (Table 1), suggesting that pentacoordinated intermediates favor the basal configuration (precursor to the *mer*-product).

One interesting point concerning the manganese complexes studied here is that, although the chromophore corresponds to the MLCT transition having high absorptivity in the visible region, the reaction apparently occurs from a spectroscopically non-detectable state. This behavior is similar to that of $[Ru(NH_3)_5py]^{2+}$ complexes, where MLCT excited states are achieved by direct excitation, whereas the reactions often occur from a non-observable ligand field state [1–4]. The reactivity of the Ru(II) complexes depends on the relative energies of the MLCT and LF states: reactive complexes, have MLCT states with energies substantially higher than their LF bands, whereas the unreactive complexes have MLCT absorption bands at higher wavelengths than the LF bands. The same pattern was found for $W(CO)_5$(py-X) complexes [39,40]. Similarly, it may be concluded that the MLCT states for *fac*-$[Mn(CO)_3$(phen)(Im-L)$]^+$ complexes are unreactive and the LF type states are responsible for photoisomerization.

4.2. Photophysics

An energy level diagram summarizing the experimental observations is shown in Fig. 6. The relative positions of the π–π* states of phenanthroline (free and as ligand) and the MLCT states of the complex identified in the absorption spectra are depicted in the diagram. For free phenanthroline at room temperature, only the fluorescence emission is observed, whereas at 77 K phosphorescence from the triplet state can also be seen. The energies of the spectroscopic states of phenanthroline suffer little change when in the complex coordinated to the central Mn ion. Nevertheless, its fluorescence is practically totally quenched due to heavy-atom effect which increases the intersystem crossing rate constant (k_{isc}) and, as expected, phosphorescence originated from the triplet state of the ligand can be observed at low temperatures.

On the other hand, practically no emission originated from the MLCT state of the complex is observed when the initial excitation is put into the states of the ligand, indicating that the states corresponding to the ligand are reasonably orthogonal to those of the complex. When exciting the MLCT state (at ~370 nm) a broad emission peak is observed between 450 and 550 nm, at room temperature and 77 K, as well as when changing the solvent.

The emission intensity of the complex excited at 370 nm is red-shifted and weaker in MeOH compared to that in dichloromethane, confirming the MLCT character of the states involved. The larger interactions between the MLCT* state and the more polar MeOH will increase the rate of the non-radiative decay as well as shift the emission towards longer wavelengths. As in dichloromethane, the high energy excitation of the complex at 260 nm, does not lead to practically any emission due to the heavy metal induced intersystem crossing to the ligand triplet state.

Multiple emission has been reported from *fac*-$[Re(CO)_3(L_2)X]$ complexes with X=Cl, Br, I or py and L=1,10-phenanthroline, 4,4-bypyridine, 4-phenyl pyridine, 3-benzoyl pyridine, quinoline or isoquinoline [5,9,10–12,14]. At 298 K, the emission was attributed to a MLCT state, but at 77 K, the emitting state was shown to have substantial $^3\pi$–π* character. On the other side, for the *fac*-[Mn(phen)$(CO)_3$(Im-L)$]^+$ complexes studied here, the phenanthroline and MLCT emissions were only observed when excited in the respective manifolds. The independence of both emissions indicates that interconversion between the emitting states is relatively slow compared to other deactivation routes of these states and implies that the character of these excited states are somewhat different.

Luminescence at room temperature from other Mn complexes, like Mn(phen)$(CO)_3$Br was never reported. The failure to emit can be rationalized comparing the energies of the corresponding MLCT* and $^3\pi$–π* states of that complex and Mn(phen)$(CO)_3$(Im-L)$^+$. Both complexes present MLCT transitions to phen ligand. Since bromide is more electronegative than manganese, the bromide 2p orbitals will lie at a lower energy than the metal 3d orbitals. Therefore, in this case, the bonding π orbital will have a larger contribution of the bromide orbital than from the metal orbital, and conversely the anti-bonding π* orbital will have a larger contribution of the metal orbital. Thus, the lowest-energy

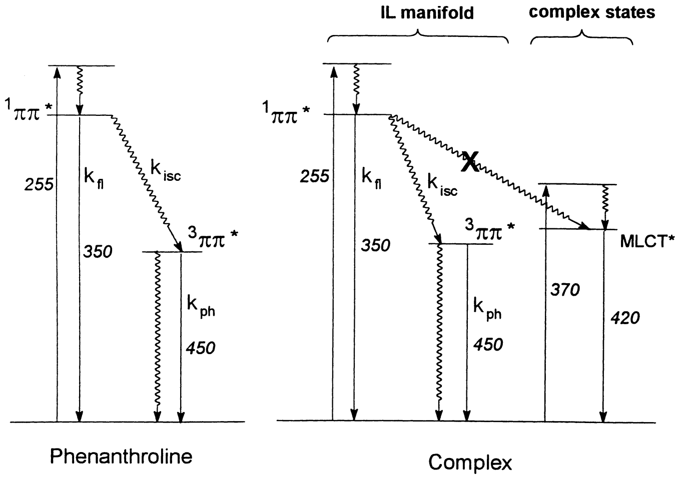

Fig. 6. Energy level diagram for phenanthroline and the *fac*-complex.

singlet state will have a larger halide character, so that corresponding transition to the excited state could be described as a $Br^{-}\rightarrow$phen XLCT transition. It should be noted that the π-donor ability of the bromide ligand lowers the energy of the MLCT excited state by increasing the negative charge on the metal.

By contrast, replacement of the bromide by imidazole, increases the attraction between the metal and the phenanthroline ligand strengthening this bond. This leads to an increases of the intensity of the visible absorption, as well as a shift to shorter wavelengths. In addition, imidazole has sufficiently high ligand-field strength to keep the ligand-field excited state at high energy. Thus, in the case of the imidazole complex the low-lying level will have MLCT character, as proved by the remarkable similarity of the shape and energy of the emission and excitation spectra of the complex in CH_2Cl_2. The opposite is true for the XLCT/MLCT ($L{=}Br^{-}$), where no π–π* emission is detected.

Although, emission from IL manifold states has been reported for many Re(I) complexes, some others, like $Re(phen)(CO)_3X$ did not present this emission [15,16,24]. Emission of the latter complexes, even at 77 K, was assigned to originate from a low-lying MLCT state [15,16]. Also, excitation to these states did not lead to photochemical reactivity. The lack of photoreactions in fluid solutions reveals that electronic excitation of the MLCT state does not lead to a reactive state nor does it channel electronic excitation to a hot-state molecule which can yield CO substitution. In addition, it can be assumed that the high energy ligand-field state is so efficiently deactivated that no reaction will proceed from there [14–16]. Furthermore, it is worth noting that the *fac*-$[Mn(phen)(CO)_3(Im\text{-}L)]^{+}$ complexes emit from both π–π* and MLCT excited states, while the analogue Re(I) complex, *fac*-$[Re(phen)(CO)_3(Im)](SO_3CF_3)$, shows only a strong phosphorescence attributed to a MLCT low-lying excited-state [24].

5. Conclusions

The results obtained for *fac*-$[Mn(phen)(CO)_3(Im\text{-}L)]^{+}$ are surprising in view of the previous studies described for Mn(I) complexes [17–21]. First, a very efficient photoisomerization process was observed upon irradiation with UV–VIS light. Despite the low-lying MLCT absorption, the excited state isomerism is consistent with a ligand-field lowest energy excited state.

In addition, these complexes emit from two non-interconvertible excited states (ππ* and MLCT). Furthermore, the emission properties can be altered by varying the solvent polarity and excitation wavelength.

The results obtained in this work reveal a number of interesting trends. The most remarkable feature of these results is the reversal of the magnitudes of MLCT and IL emitting states on going from 260 to 370 nm light excitation, solvent and temperature.

This alteration of the excited state character results in large changes in emission spectra which suggest the use of these complexes as environment probes and for electron- and energy-transfer reactions in metal transition complexes.

Acknowledgements

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