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Spectroscopic Behavior of a New Family of Mixed-ligand Iridium(III) Complexes

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Abstract

We report the results concerning the absorption spectra, luminescence spectra and luminescence lifetimes of the complexes $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(bpy)Cl}]\text{Cl}$ (**1**), $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(phen)Cl}]\text{Cl}$ (**2**), $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(bpy)H}]\text{BPh}_4$ (**3**) and $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(phen)H}]\text{BPh}_4$ (**4**) (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline and $\eta^5\text{-Me}_5\text{C}_5$ = pentamethylcyclopentadienyl = Cp*). For all complexes examined the low energy absorption band is assigned to metal-to-ligand charge-transfer transitions involving the diimine ligands. For the hydrido complexes **2** and **4** the luminescence observed both at 77 K and at room temperature is assigned to metal-to-ligand charge-transfer transitions involving the diimine ligands. The chloride complexes **1** and **3** were not found to emit.

Introduction

There is currently significant interest in the study of the thermal and photochemical activation of small molecules (e.g. CO_2, CO, H_2O) with the aim to obtain valuable fuels from raw materials [1]. It is well known that the photochemical activation shows important advantages compared with the thermal activation because it requires milder experimental conditions, thereby preventing side reactions and resulting in cleaner processes [2]. Transition metal compounds are known to induce a variety of catalytic processes through photochemical steps of different nature [3]. For many of these processes, the photochemical step has been proved or suggested to be an electron transfer step induced by light excitation which increases the redox power of the transition metal complexes. In order to work as an electron transfer photocatalyst, a coordination compound must satisfy important photophysical requirements [4], besides exhibiting high stability in the ground and excited states and suitable ground and excited states redox potentials, e.g. its lowest excited state must exhibit luminescence emission even in fluid solution at room temperature and must have a lifetime long enough to allow the participation of the excited state in bimolecular processes. The efficient photocatalytic activity in the water gas shift reaction recently shown by new Ir(III) complexes [5] prompted us to study their photophysical behavior.

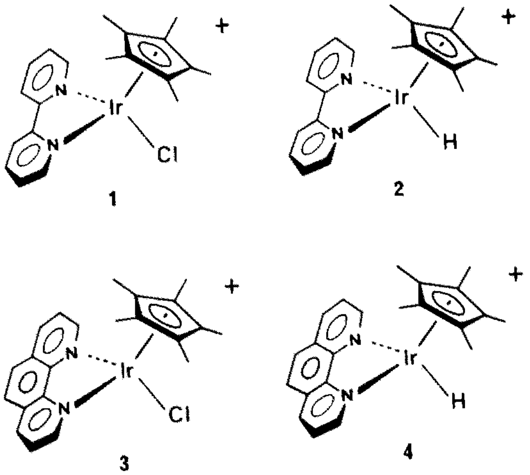

Fig. 1. Structural formulae of the iridium(III) complexes.

We report here the results concerning the absorption spectra, luminescence spectra and luminescence lifetimes of the complexes $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(bpy)Cl}]\text{Cl}$, $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(phen)Cl}]\text{Cl}$, $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(bpy)H}]\text{BPh}_4$ and $[(\eta^5\text{-Me}_5\text{C}_5)\text{Ir(phen)H}]\text{BPh}_4$ (Fig. 1).

Experimental

The synthesis, purification, molecular and single crystal structure of the complexes have been previously reported [6]. Freshly distilled acetonitrile spectroscopic grade and butyronitrile were used as solvents. When necessary the solutions were deaerated by repeated freeze–pump–thaw cycles. All manipulations of the hydrido complexes were performed in an inert (Ar) dry-box atmosphere. The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. Emission spectra (uncorrected)

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were obtained with a Perkin-Elmer LS5 spectrofluorimeter equipped with a Hamamatsu R 928 phototube. Emission lifetimes were measured with the same spectrofluorimeter working in phosphorescence mode and with an Edinburgh 199 DS single photon counting equipment. Single exponential decays were obtained in all cases. The estimated error was ⩽10%.

Results

The chloride complexes **1** and **3** are stable in the dark in the solvents used for at least one day. Since the hydrido complexes **2** and **4** are highly sensitive to oxygen, all manipulations were performed in deoxygenated solvents and inert atmosphere. Under such conditions the hydride solutions are stable for few hours. The absorption spectra of the four complexes in AN solution, at room temperature, are shown in Figs. 2 and 3. The wavelength and the extinction coefficient of the maximum of the bands are given in Table 1. The chloride complexes do not show luminescence emission either at room temperature or at 77 K. On the contrary, both hydrido complexes show a strong luminescence at 77 K with maximum at 600 nm and lifetime of 18 μs and 27 μs for [(η^5-

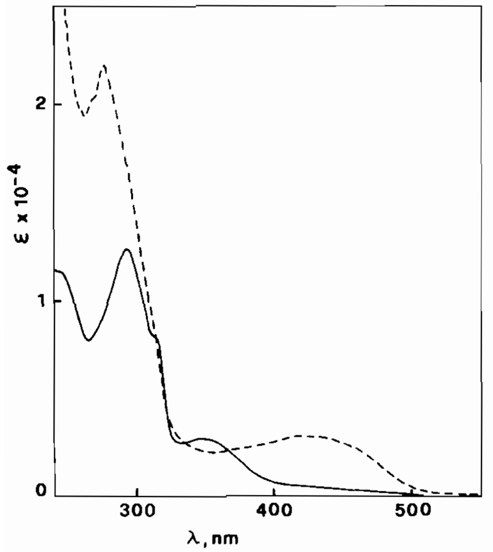

Fig. 2. Absorption spectra of [(η^5-Me_5C_5)Ir(bpy)Cl]$^+$ (——) and [(η^5-Me_5C_5)Ir(bpy)H]$^+$ (- - - -) in AN solution.

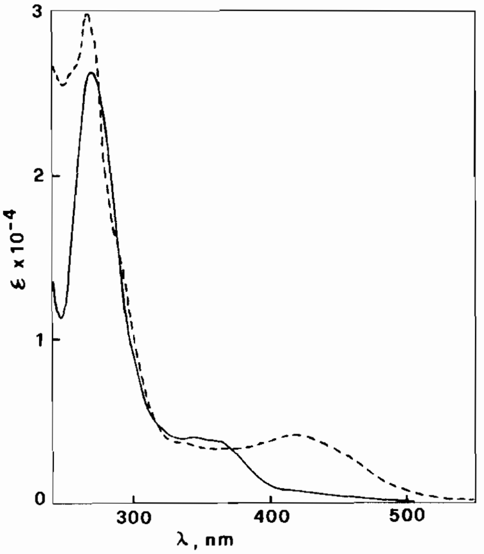

Fig. 3. Absorption spectra of [(η^5-Me_5C_5)Ir(phen)Cl]$^+$ (——) and [(η^5-Me_5C_5)Ir(phen)H]$^+$ (- - - -) in AN solution.

TABLE 1. Absorption and emission data for Ir(III) complexes

Complex	Absorption[a] 293 K		Emission			
			77 K[b]		293 K[a]	
	λ (nm)	(ε (M^{-1} cm^{-1}))	λ[c] (nm)	τ[d] (μs)	λ[c] (nm)	τ[d] (ns)
[(η^5-Me_5C_5)Ir(bpy)Cl]$^+$	294 312sh 351	(12500) (8000) (2900)	e		e	
[(η^5-Me_5C_5)Ir(bpy)H]$^+$	276 428	(22000) (3000)	600	18	665	80
[(η^5-Me_5C_5)Ir(phen)Cl]$^+$	270 346 362	(26000) (4000) (3850)	e		e	
[(η^5-Me_5C_5)Ir(phen)H]$^+$	268 420	(30000) (4200)	600	27	665	190

[a]Acetonitrile solution at 293 K. [b]Butyronitrile matrix. [c]Maximum of the phosphorescence emission. [d]Estimated error ±10%. [e]No emission was observed.

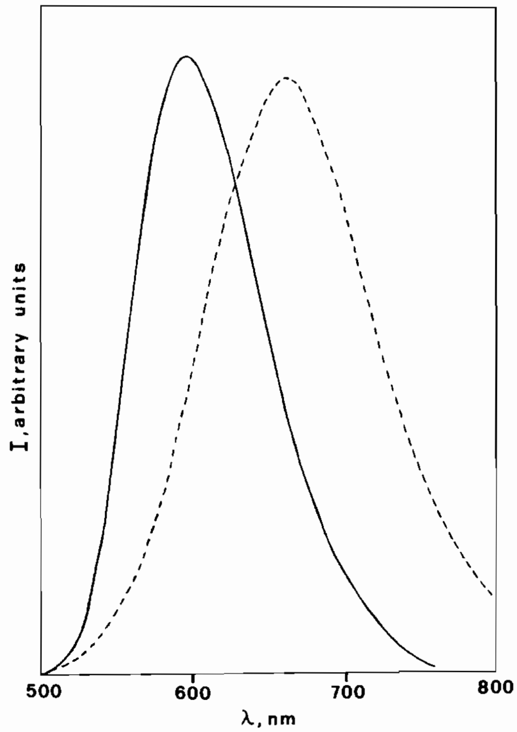

Fig. 4. Emission spectra of $[(\eta^5\text{-Me}_5C_5)Ir(phen)H]^+$ in butyronitrile matrix at 77 K (——) and in AN solution at room temperature (- - - -).

$Me_5C_5)Ir(bpy)H]^+$ and $[(\eta^5\text{-Me}_5C_5)Ir(phen)H]^+$, respectively. In fluid solution the emission shifts to longer wavelengths, becomes much weaker and the lifetime shorter (see Table 1). The emission spectra of $[(\eta^5\text{-Me}_5C_5)Ir(phen)H]^+$ in AN at room temperature and in butyronitrile at 77 K are reported in Fig. 4.

Discussion

To facilitate the assignment of the absorption bands a comparison with the spectra of $Ir(bpy)_2Cl_2^+$ [7] and $Ir(phen)_2Cl_2^+$ [8] is most useful. As one can see from Figs. 2 and 3, $[(\eta^5\text{-Me}_5C_5)Ir(bpy)Cl]^+$ and $[(\eta^5\text{-Me}_5C_5)Ir(phen)Cl]^+$ exhibit very high intensity bands in the near UV spectral region, that correspond quite well to those shown by the Ir(III) dichloro complexes and assigned [7, 8] to metal perturbed π–π^* transitions involving the diimine ligands. Above 330 nm, the two complexes show broad and relatively intense bands with maximum at 351 nm for **1** and 346 and 362 nm for **3**. These bands are similar in shape and intensity, but blue-shifted by ~1000 cm^{-1}, to those shown by the Ir(III) dichloro complexes, attributed to metal to ligand charge transfer (MLCT) transitions involving the diimine ligands. Since the π LUMO is expected to be lower in energy for bpy or phen ligands than for Cp*, due to the delocalization over a more extended aromatic system, the lowest energy bands of our complexes can also be attributed to MLCT transitions involving the diimine ligands. The little blue shift compared with the bands of the Ir(III) dichloro complexes could be due either to an increase in energy of the diimine π LUMO, or to a lowering of the energy of the metal d HOMO orbitals caused by the interaction with Cp* ligand. Since Cp* (as well as bpy and phen) is a π acceptor while Cl^- is not, when one chloride and one diimine ligand are simultaneously replaced by Cp* the net effect is expected to be an increase of the π-backbonding, and thus a lowering of the energy of the metal d HOMO orbitals. For $[(\eta^5\text{-Me}_5C_5)Ir(phen)Cl]^+$ an absorption due to the lowest energy ligand centered bands of coordinated phen [9] can also be noted in the region around 350 nm. For cyclopentadienyl complexes the d–d bands are expected to lie in the same energy region as those of the Ir(III) dichlorides [8], due to the high ligand field strength of the cyclopentadiene ring [10], further enhanced by the complete replacement of the hydrogens with electron-donating methyl groups [11].

The absorption spectra of the hydrido complexes compared with those of the analogous chlorides show small changes in the UV region and a red shift of ~5000 cm^{-1} for the lowest energy band (see Figs. 2 and 3). Such changes can be explained considering the stronger σ-donor ability of H^- compared with Cl^- that is expected to increase the negative charge of the metal, thereby displacing the metal to ligand charge transfer excited states to lower energy. Thus, the bands at 428 nm for **2** and at 419 nm for **4** may correspond to the bands exhibited by the analogous chloride complexes in the region around 350 nm, and can again be attributed to MLCT transitions involving the diimine ligands. The changes in the UV region could be due to the appearance (at lower energy) of MLCT transitions involving the cyclopentadienyl ligands. For the phenanthroline complexes it can be noted that the replacement of the chloride by the hydrido ligand does not cause the disappearance of the absorption bands in the region around 350 nm. This can be explained considering that the LC contribution to this band (see above) remains at the same energy. Concerning the d–d bands, in the hydrido complexes they are expected to lie at higher energy than for the analogous chlorides, due to the higher ligand field strength of H^- compared with Cl^- [12].

It is well known that for coordination compounds the luminescence emission can arise from LC, MLCT or MC transitions. For $[(\eta^5\text{-Me}_5C_5)Ir(bpy)H]^+$ and $[(\eta^5\text{-Me}_5C_5)Ir(phen)H]^+$ the assignment of the luminescence emission to a LC transition can be excluded in view of the following considerations: (i) the energy and the shape of the luminescence bands is completely different from that of the free diimine ligands [7, 13]*; (ii) the emission lifetimes at 77 K (18 and 27 μs respectively) are much shorter than the lifetimes of spin forbidden LC excited states, even if perturbed by a heavy atom; (iii) the red shift of the emission spectra in fluid solution at room temperature, compared with the 77 K spectra, is much larger (~1600 cm^{-1}) than that usually observed for LC transitions. The assignment of the observed emission to either MLCT or MC excited state is less straightforward. In favour of a MLCT transition are: (i) the splitting between the energies of the lowest absorption maximum, attributed to a MLCT transition, and the emission maximum (~7000 cm^{-1}, a reasonable value for CT transitions); (ii) the emission at room temperature (a feature not usually expected for d–d distorted excited states [14]); (iii) the lack of emission for the analogous chloride complexes, in spite of the presence of lower MC states.

Therefore for the hydrido complexes the assignment of the luminescence emission to a MLCT transition involving the diimine ligand can be confidently made. For the chloride complexes the lack of luminescence, both at 77 K and at room temperature, can be explained taking as the lowest excited state a distorted MC state which undergoes fast radiationless decay even at 77 K.

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LC transitions involving Cp have not been taken into account since they are expected to be at higher energy than those involving the diimine ligands.