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SPECTROSCOPIC PROPERTIES OF Pt(II) and Pd(II) COMPLEXES WITH AROMATIC TERDENDATE (C^N^C) CYCLOMETALLATING LIGANDS

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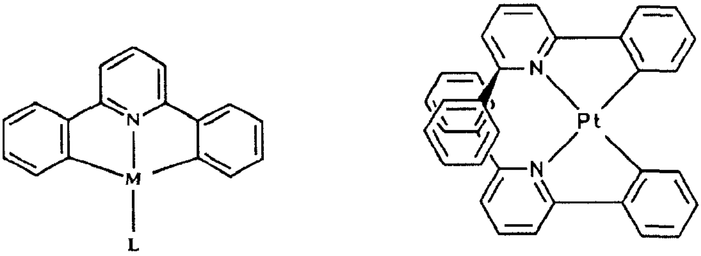
Abstract

Emission spectra, emission lifetime and electrochemical behavior of the complexes Pt(H-dppy)$_2$, Pt(dppy)S(Et)$_2$, Pt(dppy)py, Pt(dppy)pyr, (dppy)Pt-pyr-Pt(dppy), and Pd(dppy)py (where dppy^{2-} is the C$^-$ deprotonated form of 2,6-diphenylpyridine and py and pyr are pyridine and pyrazine) have been studied. The structured luminescence spectra observed at 77 K have been assigned to transitions having i) MLCT character in the case of Pt(H-dppy)$_2$, ii) mainly MLCT character with some LC contribution for the four tridentate *trans* Pt(II) complexes and iii) almost pure LC character for the Pd(II) complex. The luminescence emission involves in all cases the dppy ligand even though the electrochemical results suggest a LUMO orbital centred on the pyrazine ligand in the Pt(dppy)pyr complex and on the metal in the Pd(dppy)py complex.

Introduction

The study of the photochemical and photophysical properties of transition metal complexes is of great interest for theoretical and practical applications [1-4]. In the past 20 years, most of the attention in this field has been focussed on complexes of the polypyridine-type family [5-8]. A few years ago, we (and others) [9-11] began a systematic study of the excited state behavior of cyclometallated complexes due to the structural similarity between cyclometallating and polypyridine ligands, the higher ligand field strength of C$^-$ compared to N, the large number of metal ions (some also in different oxidation states) that give rise to stable cyclometallated compounds, and the interesting isomeric situations that can be encountered. Among the various complexes studied so far, an important part is constituted by square planar bis-cyclometallated Pt(II) and Pd(II) complexes [11]. They all have *cis*–configuration [12-14]; there is a very strong tendency to form the *cis*–compound, probably due to the strong *trans* effect of the C-ligand.

C,C-*trans*-bis-cyclometallic complexes can only be prepared [15] with tridentate (C^N^C) ligands such as 2,6-diphenylpyridine (dppy), a ligand analogous to terpyridine, but with two carbon donor atoms. We have prepared a series of *trans* complexes with this ligand with the aim of comparing the spectroscopic behavior of *cis* and *trans* cyclometallated planar complexes.



M(dppy)L   Pt(H-dppy)$_2$

Fig. 1 - Structural formulae of the complexes studied (M = Pt, Pd and L = S(Et)$_2$, py, pyr)

Experimental

The preparation purification and characterization of Pt(H-dppy)$_2$, Pt(dppy)S(Et)$_2$, Pt(dppy)py, Pt(dppy)pyr, (dppy)Pt-pyr-Pt(dppy), and Pd(dppy)py have been reported previously [15]. Polarographic grade, acetonitrile (AN), and spectroscopic grade CH_2Cl_2, MeOH and EtOH were used as solvents. Low temperature measurements (77 K) were performed in 1:5 v/v MeOH/EtOH. When necessary the solutions were deaerated by repeated freeze-pump-thaw cycles.

The absorption spectra were recorded with a Kontron-Uvicon 860 spectrophotometer. Emission spectra (uncorrected) were obtained with a Perkin-Elmer LS50 spectrofluorimeter equipped with a Hamamatsu R 928 phototube. Emission lifetimes were measured either with an Edinburgh 199 DS single photon counting equipment or with the Perkin-Elmer LS50 spectrofluorimeter working in the phosphorescence mode.

Electrochemical measurements were carried out in AN solution with 0.1 M TEAP as supporting electrolyte by means of an Amel oscillographic polarograph 448. The working electrodes were a hanging Hg electrode and a Pt electrode for cathodic and anodic processes, respectively. The potential values reported are *vs* SCE.

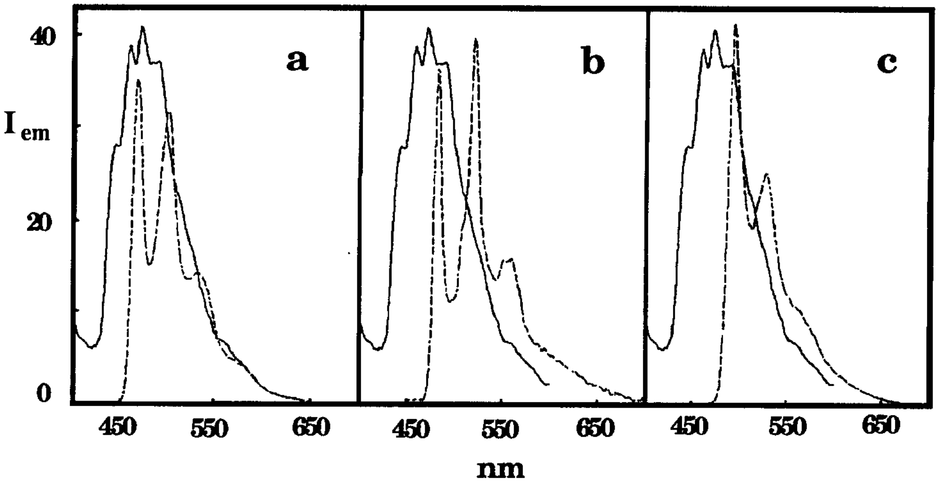


Fig. 2 - Emission spectra in MeOH/EtOH at 77 K of the (——) dppy free ligand and of (- - -): a) Pd(dppy)py, b) Pt(dppy)py and c) Pt(H-dppy) $_2$

Table - Absorption, emission and electrochemical data of the complexes studied and of the dppy free ligand.

	Absorption[a]		Emission[b]		E_p (V)[c]	
	λ(nm)[d]	ε	λ (nm)[e]	τ(μs)[f]	0/-	0/+
c-Pt(H-dppy)$_2$	404	2600	490	11	-1.98	+0.85[g]
t-Pt(dppy)S(Et)$_2$	348	13100	482	21	-1.85[h]	+1.04[g,h]
t-Pt(dppy)py	348	8400	482	20	-1.98[h]	+0.95[g,h]
t-Pt(dppy)pyr	346	13300	482	18	-1.58[h]	+1.04[g,h]
t-[Pt(dppy)]$_2$pyr	346	13300	482	18	-	-
t-Pd(dppy)py	380	8400	460	740	-2.4[g,h]	+1.20[g,h]
dppyH$_2$	320	22800	440	2.5×10^6	-	-

a) CH_2Cl_2, 293 K; b) MeOH/EtOH 1:5 v/v, 77 K; c) peak potentials in AN, TEAP 0.1 M, *vs* SCE; d) wavelength of the lowest energy absorption maximum; e) wavelength of the highest energy feature of the phosphorescence emission; f) Emission lifetime values; g) irreversible wave; h) ref 22.

Results

The complexes studied are thermally stable in the solvents used, during the time periods of the experiments. All the complexes show structured luminescence emission at 77 K in MeOH/EtOH mixture. The luminescence spectra of $dppyH_2$, Pd(dppy)py, Pt(dppy)py, and $Pt(H\text{-}dppy)_2$ at 77 K in the alcoholic mixture are reported in Fig. 2.

The highest energy feature of the emission spectra of the complexes and of the $dppyH_2$ ligand are gathered in the table together with the corresponding emission lifetime. In the Table are also reported some absorption and electrochemical data.

$Pt(dppy)S(Et)_2$ and Pt(dppy)py also exhibit luminescence (highest energy feature at 485 nm in both cases) at room temperature in deareated CH_2Cl_2 solutions with lifetimes of 54 ns and 82 ns, respectively.

Discussion

For the sake of simplicity, we discuss the spectroscopic properties of the complexes examined in the frame of the 'localized molecular orbital configuration' approach [16,17][metal-centered (MC), ligand-centered (LC), and charge-transfer (CT) transitions] even though this simplified picture is not fully satisfactory for the following reasons: i) the cyclometallated complexes exhibit a large degree of covalency of the metal-C bonds of the ground state and ii) excited-state configurations of different nature (LC and CT excited configurations) are sufficiently close in energy to be intermixed.

In complexes of metals in low oxidation states, like Pd(II) and Pt(II), ligand-to-metal charge transfer (LMCT) transitions cannot be responsible for the observed luminescence. Even MC excited state can be excluded since in the very rare cases of emission they exhibit large and unstructured bands [18]. Thus structured bands like those exhibited by the complexes examined (Fig. 2) can only be due to emission from LC or MLCT excited states. Distinction between these types of transitions is usually based on the following criteria:

i) Energy. LC luminescence is only slightly red-shifted from the emission of the corresponding free-protonated ligand. The larger is the energy (red)-shift, the higher is the MLCT character of the emitting excited state.

ii) Lifetime. LC luminescence is less sensitive to the presence of the (heavy) metal atom than MLCT emission. Thus, the longer is the radiative lifetime, the purer is the LC character of the emitting excited state.

iii) Solvent dependence. The energy of MLCT transitions is expected to depend on the solvent polarity because of the change in the dipole moment of the molecule, whereas LC transitions are expected to be less influenced by the solvent. In a rigid matrix, however, the solvent effect may be very small even for MLCT transitions.

On the basis of the above criteria we will try to assign the emission spectra of the complexes examined to specific transitions.

The *cis*-Pt(H-dppy)$_2$ complex shows an emission spectrum at 77 K with the following characteristics: i) two structured bands, ii) the highest energy feature red-shifted from that of the free ligand of about 2300 cm^{-1}, and iii) emission lifetime of 11 μs. This behavior resembles that of the *cis* Pt(II) complexes previously investigated [19-21] and points to an MLCT assignment of the emitting excited state. It has to be noted, however, that the dppy ligand has a π system that is more expanded than is that of ligands like ppy; for this reason LC excited states are lower in energy and closer to MLCT states. Consequently, the MLCT character of the emitting excited state, presumably, is less pure in this complex, than in the previously studied *cis* complexes.

The four terdentate Pt(II) complexes studied have an identical behavior. The emission spectra at 77 K of Pt(dppy)S(Et)$_2$, Pt(dppy)py, Pt(dppy)pyr and (dppy)Pt-pyr-Pt(dppy) exhibit the following characteristics: i) three well resolved bands (at the same energy in all cases) ii) the highest energy feature is red-shifted from that of the free ligand of about 2000 cm^{-1}, and iii) the emission lifetime is about 20 μs (see Table). This behavior suggests that the emitting excited state is again MLCT in nature with some LC contribution due to the relatively small red-shift of the emission energy with respect to that of the free ligand. It is evident from the red-shift and from the lifetime values (see Table) that in these complexes the emitting excited states possess a greater degree of LC character than does the *cis*-Pt(H-dppy)$_2$ complex. While this could be due, in principle, to the different geometry of the complexes (*trans* vs *cis*), we believe that this is a result of a lower ligand field strengh of the *trans* compared with the *cis* complexes, caused by the rigidity of the terdentate ligand, which is not able to coordinate the metal in the proper way. An X-ray structure determination of Pt(dppy)py [22] has shown that the Pt-C bond distances are longer in the *trans* than in the *cis* complexes. This prevents a good interaction between metal and ligand with two consequences i) decrease of the ligand field strength and ii) decrease of the energy of the HOMO d orbital (which causes the observed blue-shift of the emission energy of the *trans* compared with the *cis* complexes). The identical emission spectra of the four complexes indicate that the ligand involved in the transition is the terdendate dppy ligand. This is obvious for the Pt(dppy)S(Et)$_2$ since only the dppy ligand can be involved in MLCT transitions. For the Pt(dppy)py complex both ligands could be involved, in principle, but the LUMO orbital of the dppy has to be somewhat lower in energy with respect to the LUMO orbital of the pyridine, due to the more extended π-system in the former ligand. In the case of Pt(dppy)pyr and (dppy)Pt-pyr-Pt(dppy) emission from an MLCT excited state involving dppy is surprising because of the lower reduction potential of the pyr compared to the dppy ligand. This relative energy position of the two orbitals is also confirmed by the cyclic voltammetry of the complex (see Table). The explanation for the observed luminescence behavior could be found in geometrical factors. X-ray structure determination [22] of the parent Pt(dppy)py complex has shown that while the two phenyl and the pyridine rings of the dppy ligand lie in the same (coordination) plane, the pyridine ligand is almost perpendicular to this plane. If one assumes the same structure for Pt(dppy)pyr, it can be seen that the perpendicularity of the pyrazine ring with respect to the remaining part of the molecule clearly prevents a good π interaction between Pt and pyrazine, so that the orbital involved in the MLCT (Pt--->pyr) transition may not have the correct symmetry for a transition of sufficiently strong intensity to be seen in the emission spectrum of Pt(dppy)pyr and (dppy)Pt-pyr-Pt(dppy). Moreover, the identical emissive properties of the monomeric and the dimeric pyrazine complexes suggest that in the dimetallic complex the two metal centers do not influence each other and that the bridging pyrazine ligand acts as an "innocent" bridge.

The emission spectrum of the Pd(dppy)py complex is red shifted by about 1000 cm^{-1} and the emission lifetime is 740 μs. These results clearly indicate a LC nature of the emitting excited state and are in contrast with cyclic voltammetry experiments which, by exhibiting irreversible oxidation and reduction behavior, suggest a metal centered (MC) nature of the HOMO and LUMO orbitals of the complex. This is an evident case of failure of the Koopman theorem due to the very close proximity of the HOMO and LUMO orbitals of the metal and the ligand and could again be explained by the rigid nature of the terdentate dppy ligand. The smaller dimension of the Pd ion compared with Pt causes a smaller interaction with the rigid dppy ligand with the consequence of a further decrease of both the absolute energy and the energy splitting between the HOMO and LUMO d orbitals, which may actually be close to the π and π^* orbitals of the ligand.

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