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Photodynamics of organometal chelates

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Abstract

For a number of Rh^{3+} -chelate compounds in the phosphorescent triplet state ODMR and microwave recovery experiments have been performed. The excitation is found to be predominantly of $^3\pi\pi^*$ nature localized on the thienylpyridyl ligand. The spin-selective radiative decay of the triplet state is explained assuming σ -bonding between the metal ion and the ligand molecules.

In this paper we investigate the static and dynamic properties of the lowest excited triplet state in d^6 Rh^{3+} -chelates with the general formula $[\text{Rh}(\text{thpy})_x(\text{phpy})_{2-x}(\text{bpy})]^+$ ($x = 1, 2$), using optical-microwave double-resonance techniques at 1.4 K. The ligands thpy^- (= 2,2'-thienylpyridine) and phpy^- (= 2-phenylpyridine) are cyclometalating ligands, coordinated to the metal ion with one N atom and one C atom, whereas the bpy (= 2,2'-bipyridine) ligand coordinates with two N atoms. The $[\text{Rh}(\text{thpy})_x(\text{phpy})_{2-x}(\text{bpy})]^+$ cations enter a single host crystal of $[\text{Rh}(\text{phpy})_2(\text{bpy})]\text{PF}_6$ in such a way that the dopant bpy ligand is always sited at a former host bpy ligand position [1,2]. For the dopant complex with $x = 1$, the thpy^- and phpy^- ligands can occupy either of the two phpy^- positions in the crystal lattice, giving rise to two inequivalent complex conformations in the crystal lattice, denoted $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$. For the dopant complex with $x = 2$, there is only one complex conformation in the crystal lattice, denoted

$\text{Rh}(\text{TTB})^+$. Results of previous optical spectroscopic measurements on these compounds, in combination with lifetime data, strongly suggested that the emitting state is essentially a $^3\pi\pi^*$ state, localized at one thpy^- -ligand molecule [1]. However, in these experiments no definite proof about the nature of the lowest emissive state has been presented. The results of our experiments provide independent and direct evidence for the localized $^3\pi\pi^*$ character of the lowest excited (emissive) state. Moreover, from a kinetic study, information is obtained concerning intramolecular relaxation dynamics.

The crystals used in the experiments were the same as described previously [2]. Optical excitation was at 488 nm using a cw Ar^+ laser. The ODMR spectrometer for performing the optical-microwave double-resonance and microwave recovery experiments has been described elsewhere [2]. The temperature in the double-resonance experiments was 1.4 K.

Fig. 1(a) displays the high-energy part of the emission spectrum of the codoped single crystal $[\text{Rh}(\text{phpy})_2(\text{bpy})]\text{PF}_6$. Three zero-phonon lines are observed at 520.7, 519.9 and 517.9 nm, which have

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Fig. 1. (a) High energy part of the emission spectrum of 0.5% Rh(TPB)⁺/Rh(PTB)⁺ and codoped 0.25% Rh(TTB)⁺ in a single crystal of [Rh(phpy)₂(bpy)]PF₆ at 1.4 K. Excitation is at 488 nm. (b) PMDR spectrum of Rh(TTB)⁺, obtained at the 2575 MHz zero-field ODMR resonance frequency. (c) PMDR spectrum of Rh(TPB)⁺, obtained at the 3970 MHz zero-field ODMR resonance frequency. (d) PMDR spectrum of Rh(PTB)⁺, obtained at the 1480 MHz zero-field ODMR resonance frequency.

previously been attributed to originate from Rh(TTB)⁺, Rh(TPB)⁺ and Rh(PTB)⁺, respectively [1, 2]. For each of the three zero-phonon lines we could detect a zero-field optically detected mag-

netic resonance (ODMR) spectrum, of which the resonance frequencies have been reported previously [2]. From an extensive investigation of the splittings and anisotropic behavior of the ODMR

Table 1

Total decay rate constants k_i ($\times 10^3 \text{ s}^{-1}$) and relative radiative decay rates k_i^r of the doped complexes $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$. The values previously obtained for $\text{Rh}(\text{bpy})_3^+$ are also included [6]

Level	$\text{Rh}(\text{TTB})^+$		$\text{Rh}(\text{TPB})^+$		$\text{Rh}(\text{PTB})^+$		$\text{Rh}(\text{bpy})_3^+$	
	$k_i(\text{tot})$	k_i^r	$k_i(\text{tot})$	k_i^r	$k_i(\text{tot})$	k_i^r	$k_i(\text{tot})$	k_i^r
τ_y	1.33	0.22	1.69	0.3	0.83	0.11	0.15	0.1
τ_z	0.83	0.07	0.67	0.06	1.45	0.14	1.67	1
τ_x	5.26	1	5.62	1	6.06	1	0.22	0.2

transitions in the presence of externally applied magnetic fields it could be established that each ODMR spectrum is due to a photoexcited triplet state.

Of crucial importance for obtaining a good fit between the simulated curves and the experimental data is the choice of the orientation of the principal axes of the triplet state fine structure tensor. The two thpy^- positions in the lattice where thpy^- can reside, each give rise to a set of four magnetically inequivalent sites per unit cell of the crystal [3]. Computer simulations were performed for $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$ using either of these two inequivalent sets of ligand sites. Best fits are obtained for a principal axis system, designated by x, y, z in the inset of Fig. 1. For $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{TTB})^+$ satisfactory simulations of the experiments could only be obtained when it is assumed that (i) the triplet state is localized on only one thpy^- ligand in each of the two cations, and (ii) the excited thpy^- ligand is taken to occupy the same crystallographic ligand site. In $\text{Rh}(\text{PTB})^+$ the excitation is also trapped on the thienylpyridyl ligand, the position of which is now in the other non-bpy ligand site.

The emission wavelength dependence of the three aforementioned zero-field ODMR spectra was also detected. In these phosphorescence microwave double-resonance (PMDR) experiments, one is able to resolve the individual emission spectra of $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$ (cf. Figs. 1(b)–(d)), respectively. Since the vibrational progressions in the different PMDR spectra are all found to be similar, but different from that characteristic of a bpy emission, it follows that the optical microwave double-resonance spectra derive from

an electronic excitation trapped at the thienylpyridine ligand, i.e., the common ligand in each of the three complex cations.

From optically detected microwave recovery and adiabatic rapid passage experiments the kinetic properties of the triplet sublevels in $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$ were determined. Table 1 summarizes the lifetimes of the individual triplet sublevels of the three complex cations. The transients are representative of the population decay of the spin sublevels. They could be fitted to a biexponential curve of the form

$$f(t) = A \exp(-k_1 t) - B \exp(-k_2 t), \quad (1)$$

where k_i represents the total decay rate of sublevel i and the ratio A/B equals the ratio of the radiative rate constants of the resonantly excited sublevels 1 and 2. Expression (1) illustrates that at 1.4 K the resonantly coupled spin levels are thermally isolated from the bath and that in the microwave recovery experiment the superposition of the decay kinetics of the two levels 1 and 2 is monitored.

All three triplet systems display strongest radiative decay from their in-plane τ_x sublevel. Furthermore, the radiative decay of the thpy^- -localized $^3\pi\pi^*$ state in the complex cations is faster by about two orders of magnitude as compared to that for the pure ligand (35 ms for the free ligand as compared to 0.5 ms of the chelated ligand at 77 K). To account for the observed enhanced radiative behavior of the triplet sublevels, we consider selective spin-orbit interactions with energetically close lying singlet configurations of metal-to-ligand charge transfer of $^1d\pi^*$ nature. In particular, we consider singlet excitations mixed into the triplet states by H_{SO} of the form $^1(\pi + \delta d_\pi)\pi^*$ or $^1(\sigma + \delta d_\sigma)\pi^*$,

where d_π and d_σ represent d-orbitals with π - and σ -type overlap to the ligand molecular orbitals, respectively. It is straightforward to show from simple symmetry arguments [4] that singlet configurations of the form $^1(\pi + \delta d_\pi)\pi^*$ (in which the metal character is introduced via π -bonding), can mix via spin-orbit interactions only with the $^3\pi\pi^*(\tau_z)$ configuration, where τ_z is the out-of-plane triplet state sublevel. As is clear from Table 1, experimentally, this sublevel does not appear to be the most radiative triplet sublevel. On the other hand, spin-orbit-induced mixing of the $^1(\sigma + \delta d_\sigma)\pi^*$ configurations with the excited $^3\pi\pi^*$ configuration correctly predicts the experimental result, namely an emissive in-plane τ_x level of the thpy^- ligand in $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$. We thus conclude that for the three cations the metal character in the admixed singlet configurations originates in σ -bonding between the metal and the ligand.

Previously it has been discussed for the $\text{Rh}(\text{bpy})_3^{3+}$ and $\text{Rh}(\text{phen})_3^{3+}$ cations that the lowest excited state is a ligand-localized $^3\pi\pi^*$ configuration [5]. For these cations it has been discussed that the energy of singlet configurations of the type $^1\pi\pi^*$, but more relevant for our purposes, also of the type $^1(\pi + \delta d_\pi)\pi^*$ are nearest to the energy of the $^3\pi\pi^*$ configuration. Singlet configurations of the type $^1(\sigma + \delta d_\sigma)\pi^*$ are much higher in energy. Under such conditions, spin-orbit coupling preferentially mixes $^1(\pi + \delta d_\pi)\pi^*$ configurations into the $^3\pi\pi^*$ state, and consequently, one expects the out-of-plane τ_z triplet sublevel to be radiative, as was indeed verified from ODMR experiments [6]. Replacement of two diimine ligand molecules by cyclometalating ligands implies a stronger covalency of the metal-carbon σ -bond as compared to the metal-nitrogen σ -bond. In terms of a simple molecular orbital picture the stronger covalency character signifies non-negligible overlap between metal

ion e_g -type d-orbitals and ligand σ -type orbitals giving rise to σ -bonding and anti-bonding molecular orbitals. In addition, $^1(\pi + \delta d_\pi)\pi^*$ and $^1(\sigma + \delta d_\sigma)\pi^*$ configurations have comparable energy and the $^1(\sigma + \delta d_\sigma)\pi^*$ excitation may even be lowest. Consequently, it is to be expected that SO-induced mixing of the $^1(\sigma + \delta d_\sigma)\pi^*$ configuration into the $^3\pi\pi^*$ state will be appreciable. As mentioned above, mixing of $^3\pi\pi^*$ and $^1(\sigma + \delta d_\sigma)\pi^*$ configurations leads to radiative character of the in-plane τ_x level. As could be verified experimentally for the cyclometalating complexes $\text{Rh}(\text{TTB})^+$, $\text{Rh}(\text{TPB})^+$ and $\text{Rh}(\text{PTB})^+$, the τ_x level is the most radiative triplet state sublevel. In conclusion, the fact that for the latter complexes the in-plane triplet state sublevel is radiative clearly reflects the increased covalent bonding between the central metal ion and the ligand molecules.

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