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Optically Detected Magnetic Resonance in the Lowest Triplet State of $Pd(2\text{-thpy})_2$

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An optically detected magnetic resonance (ODMR) study of the lowest excited state of $Pd(2\text{-thpy})_2$ ($(2\text{-thpy})^- =$ 2-thienylpyridinate) in an *n*-octane Shpol'skii matrix at $T = 1.4$ K is reported. The results in zero and low magnetic fields allow us to characterize the emissive triplet state in more detail. In this state the spin−orbit contributions to the zero-field splittings of the triplet substates are much more pronounced than for analogous Rh(III) chelate complexes. Microwave recovery experiments display the emission lifetimes of 134 μs and 1200 μs of two triplet substates, which are split by $2E = 2886$ MHz (0.0962 cm^{-1}). The D value characterizing the relative energy of the third sublevel is larger than 6600 MHz (0.22 cm^{-1}) and is outside the microwave range of our experimental equipment. However, its decay time can be determined to be 235 μs. Moreover, phosphorescence microwave double-resonance (PMDR) experiments reveal a spin selectivity in the vibrational satellite lines of the emission spectrum. Such a phenomenon is observed for the first time for transition-metal compounds. The selectivity is a consequence of different mechanisms of radiative vibronic deactivations from the different emissive triplet sublevels.

1. Introduction

In recent years the characterization of luminescent transition metal ions coordinated by organic ligands has attracted great interest.[1−5] A deep understanding of these metal complexes is important because of their applicabilities, for example, in photocatalysis[6] and in solar energy conversion,[7] as chemical sensors[8] or biosensors,[9] and in supramolecular systems.[10] These complexes exhibit characteristic new properties which cannot be found in the pure organic molecule or in transition-metal compounds showing only dd^* transitions. Optical studies, in particular, when highly resolved spectra can be registered, provide an enormous source of information.[11−13] However, the usually obtainable optical resolution is mostly restricted to 1 or 2 cm^{-1}. Thus in some cases, for example for Rh(III) complexes, optical investigations have been complemented with ODMR studies (optical detection of magnetic resonance) of the complexes in the excited triplet state,[14−23] whereby the spectral resolution may be expanded into the range of several megahertz

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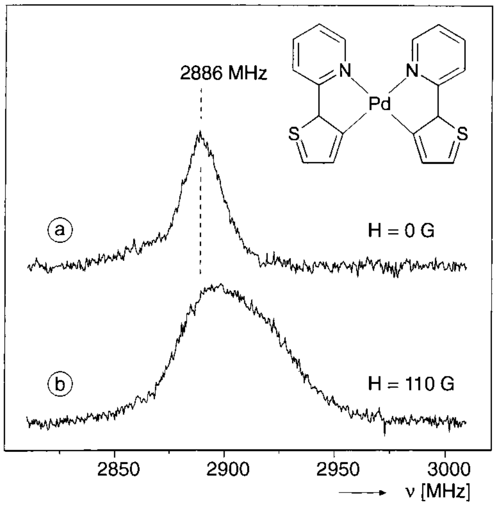

Figure 1. (a) Zero-field ODMR spectrum of Pd(2-thpy)$_2$ in an *n*-octane Shpol'skii matrix ($c = 10^{-5}$ mol/L). Conditions: $T = 1.4$ K, excitation wavelength 330 nm, detection at the electronic origin of the triplet → singlet transition at 542.95 nm (18 418 cm^{-1}). (b) ODMR spectrum under the same conditions as in (a), but in a magnetic field of $H = 110$ G.

(30 MHz $\hat{=}$ 0.001 cm^{-1}). When such double-resonance experiments are feasible, very often detailed information regarding the fine structure of the excited triplet state sublevels and the radiative properties of the substates may be obtained$^{14-23}$ (see also ref 24). For example, for some Rh(III) complexes involving heterocyclic aromatic ligands it was established that the lowest excited state is predominantly of $^3\pi\pi^*$ character with little metal-d contribution.$^{11-13,16-20,25}$ Furthermore, for these Rh(III) complexes the fine-structure splittings within the triplet states and the individual lifetimes of the triplet state sublevels at liquid helium temperatures were determined on the basis of ODMR experiments.$^{16-18,21}$

Recently, optical investigations of Pd(2-thpy)$_2$ ((2-thpy)$^-$ = 2-thienylpyridinate; see inset of Figure 1) doped into an *n*-octane Shpol'skii matrix revealed highly resolved emission spectra and showed that the phosphorescent triplet state decays with three lifetime components of $\tau_{\rm I} = 1200$ μs, $\tau_{\rm II} = 235$ μs, and $\tau_{\rm III} = 130$ μs characteristic of the triplet state sublevels.$^{26-28}$ Although the fine-structure splitting, being characteristic of the triplet state of Pd(2-thpy)$_2$, remained unresolved in the high-resolution emission spectrum, an upper limit of about 1 cm^{-1} could be given. Furthermore, time-resolved phosphorescence spectra displayed different time dependences for the vibrational satellites in the high-resolution emission spectra.^{27} This result shows a disparity in the emissive properties of the triplet state sublevels. It thus suggests that optical detection of magnetic resonance in the excited triplet state of the Pd(2-thpy)$_2$ complex might be successful. Indeed, as will be shown in this paper, the triplet nature of the emissive excited state and the zero-field splittings may be characterized in more detail using zero-magnetic-field ODMR, optically detected EPR (electron paramagnetic resonance) measurements in the presence of small magnetic fields, and pulsed microwave recovery experiments. In particular, from these recovery experiments the lifetimes of the triplet substates involved in the microwave transition may be determined. Finally, the microwave-induced changes in the emission intensity of the vibrational satellite structure, as displayed in the phosphorescence microwave double-resonance (PMDR) spectrum of Pd(2-thpy)$_2$, allows us to relate^{27}—complementary to the conclusions drawn from the optically highly resolved spectra—specific vibronically induced radiative deactivations to individual triplet sublevels.

2. Experimental Section

Pd(2-thpy)$_2$ was synthesized as described previously.^{29} Pd(2-thpy)$_2$ was first dissolved in 1,4-dioxane; thereafter the solution was diluted with *n*-octane to a ratio of 1:50 v/v. The final concentration of Pd(2-thpy)$_2$ was estimated to be 10^{-5} M. The solution was poured into a quartz cuvette and rapidly cooled in the liquid-helium cryostat to obtain a Shpol'skii matrix. For optical excitation of the Pd(2-thpy)$_2$ probe the filtered light (Schott UG-5 filter, $\lambda_{\rm exc} \approx 330$ nm) from a 100 W high-pressure mercury lamp (PEK) was used. Excitation was through the quartz windows of the helium cryostat containing the sample. The emitted light perpendicular to the excitation direction was focused onto the entrance slit of a Hilger and Watts Monospek 1000 grating monochromator and detected photoelectrically using a GaAs photomultiplier tube. The ODMR spectrometer has been described elsewhere.^{30} Microwave pulse trains of about 20% duty cycle were applied at a repetition rate of 150 Hz during a frequency scan. The microwave pulses were amplified using a traveling-wave-tube amplifier and led through a semirigid cable ending in a slow-wave helix in the helium cryostat. The liquid-helium bath was pumped down to a temperature of 1.4 K. The sample was mounted inside the helix positioned in the helium bath. The microwave-induced changes in the emission intensity of the complex were monitored using phase-sensitive lock-in detection techniques. For the microwave recovery experiments, a microwave pulse of a duration of typically 0.2 μs was applied under cw optical excitation. The ensuing transient in the optical emission was accumulated using a PAR signal averager. Magnetic fields were applied by means of superconducting Helmholtz coils, immersed in the liquid-helium bath, fed by a regulated power supply. A personal computer was used for recording, data storage, and processing.

3. Results and Discussion

Figure 1a shows the zero-field ODMR spectrum for Pd(2-thpy)$_2$ detected at the electronic origin of the emission spectrum at 18 418 cm^{-1} (542.95 nm). The microwave frequency corresponding to the peak of the signal is found at 2886 MHz; the signal line width is 20 MHz (fwhm). In the frequency range from 300 MHz up to 8000 MHz no other zero-field ODMR signal could be observed. Recently, Yersin et al.^{27} reported on time-resolved emission experiments, performed at $T = 1.3$ K, for photoexcited Pd(2-thpy)$_2$. The emission decay consists of three different decay components, and it was concluded that this emission originates from an excited triplet state for which the three substates are thermally isolated, and thus each substate displays its own decay kinetics. The ODMR transition of Figure 1a is likely to be characteristic of one of the three possible microwave transitions of the excited triplet state. Assuming two zero-field splitting parameters, *D* and *E*, several possibilities

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may be considered to account for the absence of the other transitions between the three sublevels in the zero-field ODMR spectrum:[32] (i) the resonance frequencies of the other transitions are outside the microwave range that was experimentally accessible to us (up to 8000 MHz), (ii) the disparity in the radiative decay rates of the resonantly coupled spin states is too small to make ODMR observable, and (iii) the population differences among the triplet state sublevels are too small to allow for ODMR detection. Although the optical investigations reported in ref 27 indicate that cases ii and iii should not cause problems, we have additionally attempted optically detected EEDOR (electron−electron double resonance).[32] In this experiment, a second microwave source connected to a second helix was used. The frequency of this second microwave source was swept over the range from 300 MHz up to 8000 MHz, while the frequency of the first microwave source was kept constant at the resonance frequency of 2886 MHz. In zero field, no additional lines could be observed in the EEDOR experiment for photoexcited Pd(2-thpy)$_2$. It is likely, therefore, that the other transitions are well outside the microwave frequency range applied.

To further examine this possibility of relatively large splittings, we have applied small magnetic fields (<400 G) in the normal ODMR experiment. The magnetic field will induce shifts of the triplet-state sublevel energies of the randomly oriented molecules in the Shpol'skii matrix. Figure 1b shows the ODMR signal in the presence of a magnetic field of 110 G. In addition to the slight shift of the maximum of the ODMR signal by approximately 10 MHz, the ODMR transition is broadened and asymmetrically shaped. When the magnetic field is higher than about 400 G, the ODMR signal becomes too broad (fwhm > 600 MHz) and the signal intensity too weak to allow for ODMR studies at these higher field strengths.

As discussed by McCauley and Tinti et al.[31,33] for a triplet state with $D \geq 3E > 0$ in the low-field limit, the ODMR transition in the triplet state measured for a sample of randomly oriented molecules would show a positive frequency shift (with respect to the zero-field case) for the $2E$ and $D + E$ transitions and a negative shift for the $D - E$ transition. Moreover, the $2E$ transition is expected to have its steepest rise on the low-frequency side and a larger broadening on the high-frequency wing, which leads to an asymmetric transition. The experimental result of Figure 1b is thus suggestive of a $2E$ transition and of D being larger than $3E$.

Better resolution of the microwave transition was obtained by measurement of optically detected electron paramagnetic resonance (ODEPR; e.g., see ref 34) spectra of photoexcited Pd(2-thpy)$_2$ in the *n*-octane Shpol'skii matrix. In these experiments, the microwave frequency was kept constant and the magnetic field was swept from 0 to 500 G. Amplitude modulation of the magnetic field ($H_1 = 6$ G, at the modulation frequency of 150 Hz) allowed for phase-sensitive optical detection, yielding (as in conventional EPR) a derivative signal. For various preselected values of the microwave resonance frequency the ODEPR spectra were measured and the corresponding magnetic resonance fields determined. Figure 2 is representative of the ODEPR signal measured for the microwave frequency, chosen to be 3272 MHz. Figure 3 shows a plot of the experimental results for the resonance fields as a function of various selected values of the microwave resonance frequency. The resonance spectra were also simulated as discussed in refs 35 and 36. In Figure 2 we have also included the simulated resonance signal (dashed line). It appeared that best fits were obtained for the spin Hamiltonian parameter values $|D| \geq 6600$ MHz and $|E| = 1443$ MHz, and $g \approx 2$. The best-fit simulation results are included in Figures 2 and 3. Considering the experimental errors, Figure 3 shows that reasonable agreement between the simulated and experimental results is found. It is concluded that the presented ODMR and ODEPR results are characteristic for the presence of a triplet state, of which the 2 $|E|$ splitting has been monitored.

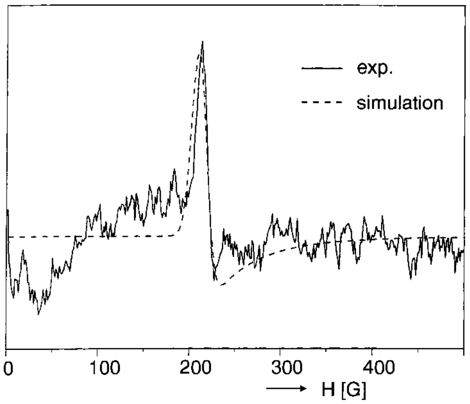

Figure 2. ODEPR of Pd(2-thpy)$_2$ in *n*-octane. Conditions: $T = 1.4$ K, excitation wavelength 330 nm, detection at the electronic origin at 542.95 nm (18 418 cm^{-1}). The microwave frequency chosen is 3272 MHz. A phase-sensitive detection with field amplitude modulation was applied ($H_1 = 6$ G, modulation frequency 150 Hz).

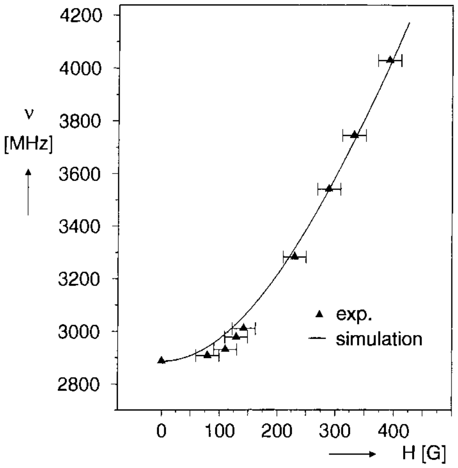

Figure 3. Magnetic field dependence of the microwave resonance frequency of the triplet state resonance of Pd(2-thpy)$_2$ in *n*-octane at $T = 1.4$ K. The solid line represents the best fit for a triplet state with the spin Hamiltonian parameter values given in the text.

The fine-structure parameter values of $|D| \geq 6600$ MHz and $|E| = 1443$ MHz, as found for the triplet state of Pd(2-thpy)$_2$, are significantly larger than the values of $D = 3440$ MHz and $E = 865$ MHz reported previously for [Rh(2-thpy)$_2$(bpy)]$^+$ and $D = 4805$ MHz and $E = 835$ MHz for [Rh(2-thpy)(2-phpy)(bpy)]$^+$.[19] In the case of the mixed-chelate Rh(III) complexes,

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it was discussed that the triplet state is mainly of $^3\pi\pi^*$ character.[19] From the anisotropic behavior of the ODMR spectra for the single crystals of these mixed-chelate rhodium(III) complexes in a magnetic field, it could be shown that the fine-structure parameters in these complexes are typical of the triplet state excitation being localized on one of the $(2\text{-thpy})^-$ ligands. In contrast to the results obtained for the mixed-chelate rhodium(III) complexes in a magnetic field,[19] little further experimental detail can be given with regards to orientation of the magnetic main axes of the $\mathrm{Pd(2\text{-}thpy)_2}$ compound. This is of course due to the fact that the simulations of the ODEPR spectra for the latter compound had to be performed for an ensemble of randomly oriented molecules in the triplet state, and thus, all information on the orientation of the magnetic axes in the molecule is lost. The larger fine-structure parameter values reported here for the excited triplet state of $\mathrm{Pd(2\text{-}thpy)_2}$ must be attributed to the influence of the transition-metal ion. More specifically, in the case of the Pd(II) complex spin−orbit interactions are more important in determining the magnitude of the fine-structure splittings than in the case of the Rh(III) complex. A similar conclusion has also been drawn from a comparison of highly resolved emission and excitation spectra of $[\mathrm{Rh(bpy)_3}]^{3+}$ and $\mathrm{Pd(2\text{-}thpy)_2}$. The importance of metal d-orbital character, which carries spin−orbit coupling, is more expressed in $\mathrm{Pd(2\text{-}thpy)_2}$ (compare refs 12, 13, 25−28, and 37 and 38). Equivalent conclusions have also been drawn by Chen et al.,[39] who studied the phosphorescent state of palladium phthalocyanines (PdPc's) in Shpol'skii matrixes. The zero-field splitting for the PdPc molecules in the triplet state (which could not be resolved in the optical experiments) was estimated to be as large as $D \approx 2$ cm^{-1} (60 GHz) and $E \approx 0$.

Further crucial information about the nature of the sublevels involved in the zero- and low-magnetic-field ODMR signals discussed above is obtained from microwave recovery experiments. In these experiments, while cw exciting the $\mathrm{Pd(2\text{-}thpy)_2}$ complex optically, a microwave pulse resonant with the zero-field transition at 2886 MHz is applied. This leads to a strong increase of the phosphorescence intensity (monitored at the electronic origin at 18 418 cm^{-1}), due to a repopulation of the sublevels involved. The recovery of the steady-state phosphorescence intensity was followed in time with a PAR 4204 signal averager.

The microwave recovery signal is displayed in Figure 4. This time-dependent signal is in good agreement with a biexponential function

$$f(t) = A \exp(-t/\tau_a) + B \exp(-t/\tau_b)$$

with $\tau_a = 134 \pm 6$ μs, $\tau_b = 1200 \pm 50$ μs, $A = 0.05$, and $B = -0.02$.

These values are in excellent agreement with the previously reported lifetimes determined in the high-resolution optical experiments.[27] The third lifetime component of 235 μs found in the latter experiments is thus not displayed in the microwave recovery signal. This tells us that the 2886 MHz microwave is resonant with the triplet sublevels $|\mathrm{I}\rangle$ (long-lived state) and $|\mathrm{III}\rangle$ (short-lived state) of the nomenclature of ref 27, while sublevel $|\mathrm{II}\rangle$ is not involved in the microwave resonance experiment.

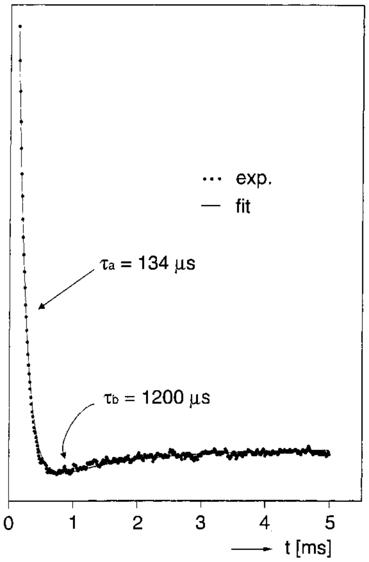

Figure 4. Zero-field microwave recovery ODMR signal of $\mathrm{Pd(2\text{-}thpy)_2}$ in *n*-octane at $T = 1.4$ K after pulsed microwave excitation. Conditions: microwave frequency applied 2886 MHz, excitation wavelength 330 nm, detection at the electronic origin at 542.95 nm (18 418 cm^{-1}). The best fit is obtained with $f(t) = A \exp(-t/\tau_a) + B \exp(-t/\tau_b)$ and $A = 0.05$, $B = -0.02$, $\tau_a = 134$ μs, and $\tau_b = 1200$ μs.

Interestingly, the time-resolved and highly resolved emission spectra[27] show that, in particular, these triplet sublevels exhibit very different emission spectra with respect to their vibrational satellite structures. The long-lived state $|\mathrm{I}\rangle$ is mainly vibronically (Herzberg−Teller, HT) deactivated, while the emission from state $|\mathrm{III}\rangle$ is dominated by vibrational satellites due to Franck−Condon (FC) activities, whereby both types of vibrational modes exhibit different frequencies. This behavior makes it attractive to measure a phosphorescence microwave double-resonance (PMDR) spectrum. In this case the intensity change of the emission induced by the microwave resonance at 2886 MHz, involving the two triplet spin levels $|\mathrm{I}\rangle$ and $|\mathrm{III}\rangle$, is measured. This spectrum (Figure 5) was recorded by keeping the amplitude-modulated microwave frequency at the constant value of 2886 MHz and detecting the emission spectrum using phase-sensitive lock-in detection. The PMDR spectrum reveals interesting intensity changes (Figure 5). By means of signal averaging detection it could be determined that, for example, the negative sign of the 229, 261, 528, and 710 cm^{-1} vibrational satellites in the PMDR spectrum corresponds to an emission intensity decrease upon inducing the microwave transition, while the positive signs at the electronic origin and the 211, 376, 447, 650, and 716 cm^{-1} satellites are connected to intensity increases. Recent time-resolved optical measurements of the emission spectrum of $\mathrm{Pd(2\text{-}thpy)_2}$ have shown that, for example, the 528 cm^{-1} satellite (which results from HT activity) originates *only* from the longest living triplet spin sublevel (state $|\mathrm{I}\rangle$ with the lifetime of 1200 μs).[27] From the observation of this microwave-induced intensity decrease of the 528 cm^{-1} satellite in the emission spectrum it follows therefore that, under cw optical excitation, the steady-state population of the triplet substate with a lifetime of 1200 μs is larger than for the substate with a lifetime of 134 μs. Since the population of the level $|\mathrm{III}\rangle$ with a lifetime of 134 μs is enhanced in the microwave recovery experiment, we conclude that the modes at 376, 447, 650, and 716 cm^{-1} are more strongly coupled to the triplet sublevel $|\mathrm{III}\rangle$.

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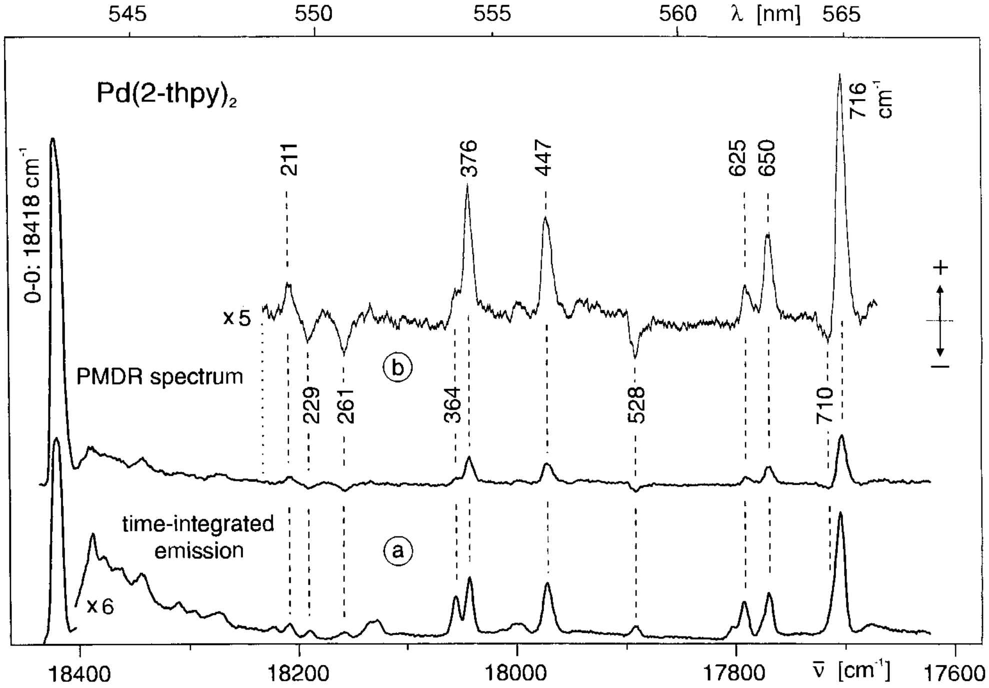

Figure 5. (a) Time-integrated emission spectrum of Pd(2-thpy)$_2$ in *n*-octane at $T = 1.4$ K and excitation wavelength 330 nm. (b) PMDR spectrum induced by a microwave resonance of the zero field transition at 2886 MHz. An intensity increase (+) signifies vibrational satellites that are connected with an emission from the short-lived triplet sublevel |III⟩, while a decrease (−) characterizes vibronic transitions from the long-lived state |I⟩.

4. Conclusion

By means of optical microwave double-resonance methods the characteristics of the emissive triplet state of the Pd(2-thpy)$_2$ complex could be studied with a spectral resolution better than 0.001 cm^{-1} (30 MHz), thus extending the resolution of recent complementary time-resolved emission studies, which exploited an optical resolution of about 1−2 cm^{-1}. In particular, from the magnitude of the zero-field splitting parameters determined for this triplet state, it could be concluded that the spin−orbit contributions to the fine-structure splittings, arising from the Pd-metal character in the triplet state, are much larger than those found for analogous Rh(III) metal chelate complexes.[19,20] Furthermore, a phosphorescence microwave double-resonance (PMDR) spectrum, resolving the vibrational satellite structure, revealed spin selectivity in the vibrational satellites of the emission spectrum, for the first time for a transition-metal complex. The results obtained for the specific vibronic deactivation paths from the different emissive triplet sublevels may be well-correlated to previously published time-resolved emission spectra.

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