Depending on excitation wavelength, the spectra can be very simple or quite complex. However, in all cases, a relatively small number of sites, some probably with distributions of their own, can be used to fit all observed spectra. This indicates that remarkably few sites are present or that the spectra of the different sites are narrow enough to permit selective excitation of a relatively small number of sites at any one time.

The wide differences in emission behavior of our complexes are explained on the basis of several criteria. We suggest that criteria can be used to fabricate systems that can show enhanced microscopic site selectivity.

The relatively small number of sites coupled with the narrowness

of the 77 K spectra suggests that these systems are candidates for Shpol'skii spectra or fluorescence line narrowing. Particularly promising are spectra measured from hydrocarbon glasses at lower temperatures than we can currently reach.

Excited-State Annihilation Process Involving a Cyclometalated Platinum(II) Complex

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The Pt(tpy)(ppz) complex exhibits strong luminescence with a relatively long excited-state lifetime (15.3 μs) in deaerated acetonitrile solution, at room temperature and at low excitation intensity, and can be easily involved in excited-state quenching processes. The ^{3}CT excited state is, in fact, quenched (i) by oxygen ($k_q \cong 10^9$ M^{-1} s^{-1}), (ii) by the ground-state complex ($k_q = 5.7 \times 10^7$ M^{-1} s^{-1}), and (iii) by another ^{3}CT excited state in an annihilation process, which is practically diffusion controlled ($k_3 > 6 \times 10^9$ M^{-1} s^{-1}). The ground-state quenching and the annihilation process most probably occur via an excimer formation mechanism.

Introduction

The search for a transition-metal compound with suitable photochemical, photophysical, and redox properties to be used as photosensitizer in energy- and/or electron-transfer processes,[2-8] has been mainly performed within the Ru(II) polypyridine family.[5,9,10] Recently, an increasing interest in cyclometalated complexes has emerged. These compounds, which contain ligands that are structurally similar to polypyridines, have long been recognized in the literature,[8,11] but their photophysical characterization has only been reported in the last few years.[12-18]

We have already reported the photochemical and photophysical properties of cyclometalated Rh(III),[19-21] Pt(II),[13,21-24] Pd(I-

I),[21,23,25] and Pt(IV)[21,26] complexes.

Continuing our investigation in this field, we report here a cyclometalated Pt(II) complex (Figure 1), whose unusual excited-state behavior can be accounted for by an excited-state annihilation process.

This process is well-known for organic molecules,[27] but only few examples have been reported in the literature in the field of coordination compounds.[28-30]

Experimental Section

The preparation of Pt(tpy)(ppz) has been reported previously.[24] Polarographic grade acetonitrile (AN) was always used.

When necessary, the solutions were degassed by repeated freeze-pump-thaw cycles.

The absorption spectra were recorded with a Kontron Uvikon 860 spectrophotometer. Emission spectra (uncorrected) and emission quantum yields were obtained with a Perkin-Elmer LS5 spectrofluorimeter equipped with a Hamamatsu R928 phototube. Emission quantum yields were referred to an aerated Ru(bpy)$_3$$^{2+}$ aqueous solution.[31,32]

Emission lifetimes were measured with either a single-photon-counting apparatus (Edimburgh Instruments, Model 199) or a laser flash photolysis apparatus having as excitation source a JK system 2000 neodymium YAG DLPY4 laser (λ_{exc} = 355 nm, pulse half-width = 25 ns, pulse

(1) (a) University of Bologna. (b) University of Fribourg.
(2) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(3) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717.
(4) Whitten, D. G. *Acc. Chem. Res.* **1980**, *13*, 83.
(5) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
(6) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
(7) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.
(8) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.
(9) Watts, R. J. *J. Chem. Educ.* **1983**, *60*, 834.
(10) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85.
(11) Omae, I. *Chem. Rev.* **1979**, *79*, 287.
(12) Sprouse, S.; King, K. A.; Spellane, P. J.; Watts, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 6647.
(13) Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; von Zelewsky, A. *Chem. Phys. Lett.* **1985**, *122*, 375.
(14) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Santhanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153.
(15) Reveco, P.; Cherry, W. R.; Medley, J.; Garber, A.; Gale, R. J.; Selbin, J. *Inorg. Chem.* **1986**, *25*, 1842.
(16) Ohsawa, Y.; Sprouse, S.; King, K. A.; DeArmond, M. K.; Hanck, K. W.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 1047.
(17) Ichimura, K.; Kobayashi, T.; King, K. A.; Watts, R. J. *J. Phys. Chem.* **1987**, *91*, 6104.
(18) Balzani, V.; Maestri, M.; Melandri, A.; Sandrini, D.; Chassot, L.; Deuschel-Cornioley, C.; Jolliet, P.; Maeder, U.; von Zelewsky, A. In *Photochemistry and Photophysics of Coordination Compounds*; Yersin, H., Vogler, A., Eds.; Springer Verlag: Berlin, Heidelberg, 1987; p 71.
(19) Maestri, M.; Sandrini, D.; Balzani, V.; Maeder, U.; von Zelewsky, A. *Inorg. Chem.* **1987**, *26*, 1323.
(20) Sandrini, D.; Maestri, M.; Balzani, V.; Maeder, U.; von Zelewsky, A. *Inorg. Chem.* **1988**, *27*, 2640.
(21) Barigelletti, F.; Sandrini, D.; Maestri, M.; Balzani, V.; von Zelewsky, A.; Chassot, L.; Jolliet, P.; Maeder, U. *Inorg. Chem.* **1988**, *27*, 3644.
(22) Sandrini, D.; Maestri, M.; Balzani, V.; Chassot, L.; von Zelewsky, A. *J. Am. Chem. Soc.* **1987**, *109*, 7720.
(23) Maestri, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A.; Deuschel-Cornioley, C.; Jolliet, P. *Helv. Chim. Acta* **1988**, *71*, 1053.
(24) Sandrini, D.; Maestri, M.; Ciano, M.; Balzani, V.; Lueoend, R.; Deuschel-Cornioley, C.; Chassot, L.; von Zelewsky, A. *Gazz. Chim. Ital.* **1988**, *118*, 661.
(25) Maestri, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A.; Jolliet, P. *Helv. Chim. Acta* **1988**, *71*, 134.
(26) Chassot, L.; von Zelewsky, A.; Sandrini, D.; Maestri, M.; Balzani, V. *J. Am. Chem. Soc.* **1986**, *108*, 6084.
(27) Birks, J. B. *Photophysics of Organic Molecules*; Wiley: New York, 1970.
(28) Lachisc, U.; Ottolenghi, M.; Rabani, J. *J. Am. Chem. Soc.* **1977**, *99*, 8062.
(29) Indelli, M. T.; Ballardini, R.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1982**, *86*, 4284.
(30) Bignozzi, C. A.; Indelli, M. T.; Scandola, F. *J. Am. Chem. Soc.* **1989**, *111*, 5192.
(31) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
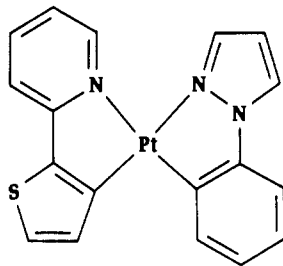(32) Nakamaru, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2697.

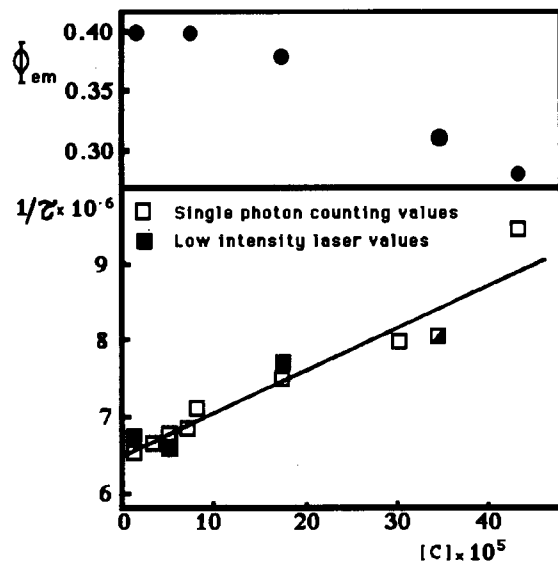**Figure 1.** Structural formula of the complex.

Figure 2. Top: Emission quantum yield vs complex concentration. Bottom: Reciprocal of the emission lifetime vs complex concentration. Intercept = 6.5×10^4 s^{-1}; slope = 5.7×10^7 M^{-1} s^{-1}.

intensity $\cong 6 \times 10^{-8}$ *Nhν*/pulse[33]) and as a detection system a Hamamatsu R928 phototube and a fast photomultiplier housing coupled with a Tektronix Model 468 oscilloscope. The laser intensity was decreased by means of liquid filters (K$_2$CrO$_4$ solutions that absorb 90%, 99%, and 99.9% of the laser beam).

Transient absorption measurements were performed by means of the laser flash photolysis equipment previously described with a Varian X 300 xenon lamp as the analyzing lamp. Proper cutoff filters were used to minimize possible photochemical processes.

Controlled-potential electrolyses were performed with an Amel Model 563 Electrochemolab instrument. The spectra of electrochemically generated species were obtained at a Pt–Rh grid used as an OTTLE (optical transparent thin-layer electrode) placed between the windows of a 2-mm spectrophotometric cell directly mounted in a Kontron Uvikon 860 spectrophotometer. The counter electrode was a Pt wire separated from the anodic compartment by a fine frit; an Ag wire acted as a quasi-reference electrode.

Results

As previously reported, Pt(tpy)(ppz) exhibits luminescence emission in both aerated and deaerated acetonitrile solutions, at room temperature. The level responsible for this emission is the lowest ^{3}MLCT excited state.[24]

The absorption and the emission spectra are practically unaffected by changing the complex concentration in the range $(1-45) \times 10^{-5}$ M.

In air-equilibrated solutions, the emission decay is strictly exponential and a lifetime of 120 ns is obtained.

In deaerated solution, the emission intensity is sensitive to the complex concentration. In fact, the emission quantum yield decreases as the complex concentration increases (Figure 2).

Even the decay of the emission intensity is found to be concentration dependent (Figure 2). In fact, the emission lifetimes,
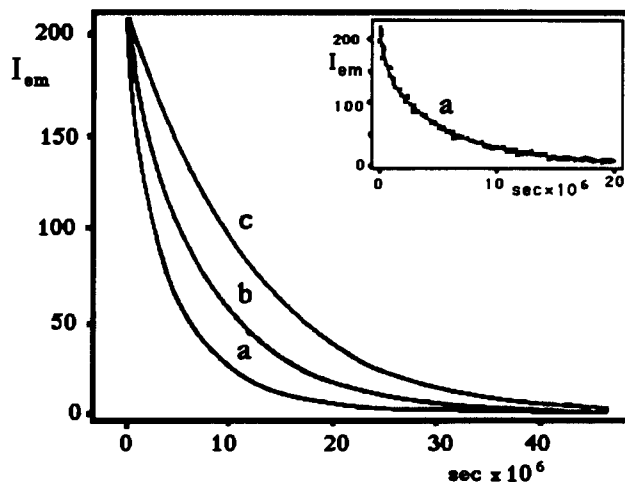
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(33) This number of photons is distributed on a sample volume lower than 0.3 mL, which means a concentration of photons greater than 2×10^{-4} *Nhν*/L for each pulse.

Figure 3. Emission decays at different laser excitation intensities of a 5.55×10^{-5} M solution of the Pt(tpy)(ppz) complex: (a) full laser power, N *hν*/pulse = 6×10^{-8};[33] (b) 10% of the laser power; (c) 1% of the laser power. Inset: Fitting of the emission decay by means of eq 2 (see text); ($\square$) experimental points from curve a; (—) calculated curve for [T]$_0$ = 5.55×10^{-5} M, $k_A = 6.8 \times 10^4$ s^{-1}, and $k_B = 4 \times 10^9$ M^{-1} s^{-1}.

measured with a single-photon-counting apparatus, decrease when the concentration increases; a plot of the reciprocal of the lifetime vs the complex concentration exhibits linear behavior with an intercept of 6.5×10^4 s^{-1} and a slope of 5.7×10^7 M^{-1} s^{-1}. If equipment based on laser excitation is used, an identical concentration dependence for the lifetime is obtained, but only at low laser intensity (Figure 2). At higher laser power, the emission decay becomes much faster (Figure 3), and at full laser power, it is clearly nonexponential. Under these conditions, the decay of the emission intensity is found to obey a mixed first-order/second-order law:

$$-d[I]/dt = k_F[I] + k_S[I]^2 \qquad (1)$$

In such a case, according to standard kinetic analyses, the following equation can be used:

$$[T]_t = k_A[T]_0/\{(k_A + k_B[T]_0)\ \exp(k_A t) - k_B[T]_0\} \qquad (2)$$

where [T]$_0$ and [T]$_t$ are the excited-state concentrations at zero time (i.e. immediately after the laser pulse) and at a time t, respectively, and k_A and k_B are the rate constants for the first- and second-order processes, respectively. Assuming that all the molecules in the laser beam are excited, [T]$_0$ coincides with the complex concentration. The emission decays at high laser power have been analyzed (nonlinear fitting) according to this assumption and to eq 2. Using a proper k_A value (i.e. $k_A = 1/\tau$ at the proper complex concentration), we have obtained k_B values ranging from 1×10^9 to 6×10^9 M^{-1} s^{-1}. Note that the lower the complex concentration, the higher the k_B value obtained; this is due to the assumption made concerning [T]$_0$, which actually approaches the initial complex concentration as it decreases. Thus, the real value for k_B is $k_B \geq 6 \times 10^9$ M^{-1} s^{-1}, a value we have obtained at the lowest complex concentration.

Laser flash photolysis experiments have shown transient absorbance changes that decayed with the same kinetics as the emission. No residual absorbance changes could be detected at any wavelength after the decay of the primary transient.

Polarographic experiments (OTTLE), aimed at detecting the spectrum of the reduced form of the complex, have shown that the monoreduced species is unstable on a time scale of minutes. In fact, reoxidation at −1.9 V of the species obtained after almost complete reduction of the complex at −2.1 V does not regenerate the initial Pt(tpy)(ppz) complex (the absorption spectrum of the reoxidized species is different from that of the initial Pt(tpy)(ppz)).

Moreover, the complex was practically photoinert in deaerated acetonitrile solution, as was demonstrated by the constancy of the absorption spectrum of a 7.2×10^{-5} M solution of the Pt(tpy)(ppz) after at least 30 pulses at full laser power.

Discussion

The reported results show that the emissive properties of Pt-(tpy)(ppz) are very sensitive to many parameters such as solution medium and excitation intensity.

The oxygen quenches the excited state of the complex very efficiently; in fact, the quenching constant is of the order of 10^9 M^{-1} s^{-1} (4×10^9 M^{-1} s^{-1}, taking $[O_2] = 2 \times 10^{-3}$ M).

Even the ground-state complex quenches its own excited state. For this process a rate constant of 5.7×10^7 M^{-1} s^{-1} is evaluated from the Stern–Volmer type plot of Figure 2. From the same plot, an inherent lifetime of 15.3 μs is calculated for the ^3CT excited state by extrapolation to zero complex concentration. This lifetime is quite long, and there is a chance for relatively efficient bimolecular reactions, such as oxygen, ground-state, and other (vide infra) quenching processes, to occur in competition with internal deactivation.

The nonexponential decay observed at high laser intensities can be ascribed to a bimolecular triplet–triplet annihilation process, as shown in the following overall kinetic scheme:

$$(^3CT)Pt \xrightarrow{k_1} (GS)Pt$$

$$(^3CT)Pt + (GS)Pt \xrightarrow{k_2} X$$

$$(^3CT)Pt + (^3CT)Pt \xrightarrow{k_3} Y$$
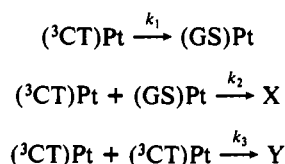
where $(^3CT)Pt$ is the triplet charge-transfer excited state of Pt-(tpy)(ppz), (GS)Pt is the ground-state complex, k_1 is the sum of all the unimolecular processes which deactivate the triplet CT excited state of the complex, k_2 is the bimolecular rate constant of the ground-state quenching process (we have seen before to be $k_q = 5.7 \times 10^7$ M^{-1} s^{-1}), and k_3 is the bimolecular rate constant of the triplet–triplet annihilation process. The validity of this kinetic scheme can be judged from the fit of the decay curve (insert of Figure 3) obtained according to eq 2 with $k_A = k_1 + k_2[(GS)Pt]$ and $k_B = k_3$.[34]

Mechanism of the Quenching Processes. Regarding the ground-state quenching, the known[24] redox potentials of the ground and excited states involved in the quenching process show that electron transfer is not possible, since it is endoergonic by about 0.8 eV. Energy transfer, even if present, would not be observable because of the recycling of the quenched excited state. Thus this, relatively fast, quenching process must be accounted for by deactivation via some other kind of interaction. While ground-state interactions are clearly not involved, since the absorption spectrum is not sensitive to complex concentration, excited-state interaction could be operative and give the observed deactivation process via the formation of an excited dimer (excimer). Even though we were unable to detect this excimer via emission spectroscopy (probably because of its radiationless deactivation[35]), we believe that two square-planar Pt complexes, one in the ground and the other in the excited state, can give, along the free axis, an interaction strong enough to form an excimer. Examples of dimeric and oligomeric species with Pt–Pt bonds have already been reported for square-planar Pt complexes both in the solid state[36] and in aqueous solution.[37] Our suggestion is also supported by the recently reported examples of inorganic exciplexes.[38-44] Some

of these examples concern planar complexes; also planar are most of the organic chromophores that are reported to form exciplexes[27] and/or excimers.[45] This fact suggests that the planar structure is particularly suited for exciplex and, even more, for excimer formation, probably because in planar molecules frontier orbitals are more exposed and readily contacted by neighboring species to give the strong interaction needed for exciplex (and excimer) formation. This also suggests that the reason for inorganic exciplexes having been almost unrecognized in the field of transition-metal photochemistry lies in the fact that octahedral complexes have been the main subject of the studies in the field of the photochemistry of coordination compounds.

As far as triplet–triplet annihilation is concerned, both electron- and energy-transfer mechanisms are thermodynamically allowed ($\Delta G = -1.4$ eV and $\Delta G = -1.1$ eV, respectively). Nevertheless, we do not accept an electron-transfer mechanism, since laser flash photolysis and laser irradiation experiments have shown that redox species (that we have demonstrated to be labile (see OTTLE experiments)) are not formed in bulk solution.[46] Neither do we accept an energy-transfer mechanism even though it is compatible with our results. In our opinion this fast annihilation process, unusual for octahedral coordination compounds for which the few reported examples are much slower,[28-30] must be related to the planar structure of the complex, which permits a strong interaction between the reaction partners, and thus has to be due to the formation of some kind of excimer as suggested for the ground-state quenching. It has to be clear, however, that the "excimers" involved in the two (ground- and excited-state) quenching processes must have quite different properties, as is suggested by the kinetic data. In particular, the inefficient ground-state quenching (about one deactivation every 100 encounters) indicates a very weak perturbation of the monomer excited state in the (singly excited) excimer. On the contrary, the annihilation process is very efficient, suggesting that some qualitatively different, fast deactivation pathway is available to the (doubly excited) excimer.

Conclusions

We wish to stress two important points that are at the basis of the unusual emissive behavior of Pt(tpy)(ppz): the relatively long excited-state lifetime and the planar structure of the complex. The quite long ^3CT excited-state lifetime gives a good chance for efficient bimolecular reactions, such as ground- and excited-state (annihilation) quenching processes, to occur in competition with internal deactivations. The relatively fast rate of these bimolecular quenching reactions is due to the planar structure of the complex, which permits a strong interaction between the reaction partners, an interaction that we believe to be sufficiently strong for the formation of an excited dimer. In fact, in our opinion, such efficient quenching processes occur via an excimer formation mechanism, particularly in the case of the ground-state quenching, where the usually considered fast quenching mechanisms, energy and electron transfer, are clearly not involved.

(34) In high-intensity measurements, such as those involved here, the ground- and excited-state quenching processes are not independent. In fact, since we are close to excited-state saturation, the ground-state concentration changes (increases) with time, going from about zero, immediately after the laser pulse, to the value of the initial complex concentration as the excited-state decay proceeds. A rigorous kinetic treatment, which takes into account the change in ground-state concentration, differs from that used here only for the value of k_B, which actually is $k_B = k_3 - k_2$ instead of the considered $k_B = k_3$. In this particular case, however, in which k_2 is much smaller than k_3, the use of the nonrigorous treatment does not affect the obtained k_3 values.

(35) McMillin, D. R.; Kirchhoff, J. R.; Goodwin, K. V. *Coord. Chem. Rev.* **1985**, *64*, 83.

(36) Biedermann, J.; Wallfahrer, M.; Gliemann, G. *J. Lumin.* **1987**, *37*, 323.

(37) Schindler, J. W.; Fukuda, R. C.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3596.

(38) Palmer, C. E. A.; McMillin, D. R.; Kirmaier, C.; Holten, D. *Inorg. Chem.* **1987**, *26*, 3167.

(39) Ayala, N. P.; Demas, J. N.; De Graff, B. A. *J. Am. Chem. Soc.* **1988**, *110*, 1523.

(40) Everly, R. M.; McMillin, D. R.; Stacy, E. M. *Abstracts*, 8th ISPPCC, Santa Barbara, CA, Aug 13–17, 1989; University of California: Santa Barbara, CA, 1989; No. C-2.

(41) Kyle, K. R.; Ford, P. C. *Abstracts*, 8th ISPPCC, Santa Barbara, CA, Aug 13–17, 1989; University of California: Santa Barbara, CA, 1989; No. C-3.

(42) Nagle, K. J.; Brennan, A. B. *J. Am. Chem. Soc.* **1988**, *110*, 5931.

(43) Stacy, E. M.; McMillin, D. R. *Inorg. Chem.* **1990**, *29*, 393.

(44) Lever, A. B. P.; Seymour, P.; Auburn, P. R. *Inorg. Chim. Acta* **1988**, *145*, 43.

(45) Kloppfer, W. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1973; Vol. 1, p 357.

(46) These results, however, do not exclude that redox species are formed[27] and then back-comproportionate within the solvent cage.