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Assignment of the triplet manifolds of d^8 complexes and linear chains via the effects of temperature and magnetic fields on the phosphorescence lifetimes

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Contents

Abstract

Characteristics of the electronic excited states of transition-metal complexes are reviewed. Attention is focussed on the experimental means of identifying the orbital natures of the emitting manifolds. Two new criteria for distinguishing among excited triplet terms are enunciated: (a) the profile of the phosphorescence lifetime vs. the temperature in the range 77–4 K, and (b) the functional dependence of the phosphorescence decay rate on an external

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magnetic field at ~4 K temperatures. These criteria are applied to the red emission emanating from solid platinum(II) complexes that form linear chains [Pt(2,2′-bipyridine)$(CN)_2$; Pt(2,2′-bipyridine)Cl_2] and to Pt(2-phenylpyridine)$_2$ that crystallizes with discrete dimeric units. The origin of the phosphorescence from all three substances is assigned to a $^3d\sigma^*p\sigma$ term from a consideration of the criteria given above. The red emission from solutions and rigid glasses of Pt(4,4′-dimethyl-2,2′-bipyridine)(ecda) and Pt(4,7-diphenyl-1,10-phenantroline)(ecda) [ecda = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate] is reassigned to a $^3d\sigma^*p\sigma$ term of a binuclear defect state since the *T*-dependence criterion does not support the current assignment to a ^{3}MLCT of a monomeric species. © 1998 Elsevier Science S.A.

Keywords: Electronic configuration; Triplet states; Platinum(II) complexes; Photophysics; Luminescence; Phosphorescence; Temperature dependence; Magnetic perturbations; Emission; Photoluminescence

1. Introduction

Knowledge of the lowest excited configurations of transition-metal complexes is necessary to design potentially important luminescent materials. Particularly for metal complexes that emit light in fluid solution there is great interest in defining their lowest emitting states, since their nature dictates the types of photochemical reactions the complexes will undergo. Metal-to-ligand charge-transfer (MLCT) excited states are especially important since they facilitate charge separation. Although the spectral characteristics and the decay time of the photoluminescence are often sufficient to identify the nature of the emitting configuration, there are cases where additional information is required to effect a definitive configurational assignment of the emitting manifold. In this contribution we delineate the roles that measurements of the temperature-dependence of the decay times and of their response to an external magnetic field have played in the characterization of the lowest excited states of binuclear complexes of Rh(I), Ir(I), and Pt(II), and we apply these criteria to assign the emitting states of solids containing linear chains of Pt(II) ions. We also offer a new view of the origin of the luminescence observed from fluid solutions of Pt(II) α,α′-diimine dithiolate complexes.

2. Supplemental criteria for defining triplet states

2.1. Temperature dependence of the phosphorescence

2.1.1. Ligand $^3\pi\pi^*$ emission

The phosphorescence emanating from formally $^3\pi\pi^*$ ligand-localized excited configurations is insensitive to temperature below 77 K until ca. 10 K. Below this temperature range the decay profile begins to deviate from exponential behavior owing to spin-polarization of the closely lying emitting triplet states. Except for a significantly shortened decay time relative to those of the $^3\pi\pi^*$ terms in most organic molecules, $^3\pi\pi^*$ manifolds in complexes behave similarly to those of the uncomplexed ligands. In a few cases these nominally $^3\pi\pi^*$ manifolds are perturbed by nearby

^{3}MLCT states and the splittings of the sublevels increase substantially [1]. This phenomenon is also revealed by the T-dependent behavior [2]. An external magnetic field splits the group of three states in a predictable way and decreases the degree of spin polarization, thus restoring exponential decay of the phosphorescence at very low temperatures [3].

2.1.2. ^{3}MLCT emission

The T-dependence of the phosphorescence emanating from these types of configurations is exemplified by the curve reproduced in Fig. 1 for the tris(bipyridine)ruthenium(II) cation (see ref. [4]; note that the published result for ϵ_2 is 56 cm^{-1}, however, these numbers were inadvertently transposed. The correct value is 65 cm^{-1}.). The phosphorescence decay retains its strict exponentiality to very low temperatures (<4 K) and therefore can be fit by the well-known equation reproduced in Fig. 2 [6].

Fitting the experimental data to this expression yields both the total rate constant of decay to the ground state of each triplet sublevel (k_1, k_2, k_3) and the two energy splitting parameters (ϵ_1, ϵ_2). Of signal importance is the fact that a satisfactory fit for ^{3}MLCT emission always requires a three-level manifold. A two-level system will not suffice [4,6,7].

Because emitting configurations of this type contain three distinct triplet states split asymmetrically, the effect of a magnetic field on the emitting manifold at $\leqslant$4 K is not simply related to the field strength but depends on the characteristics of the two upper levels and the relative magnitudes of the two splitting parameters. The

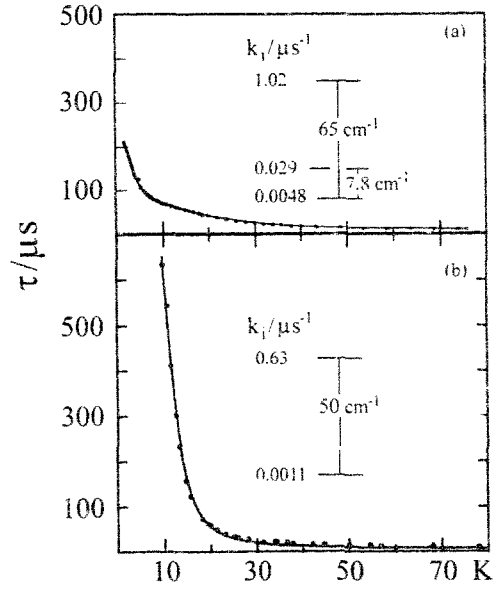
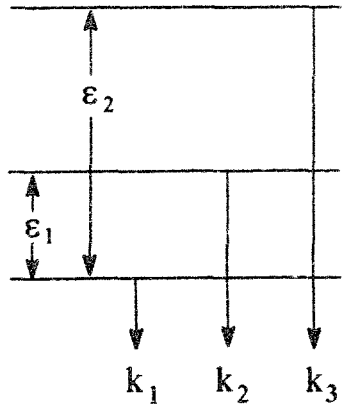


Fig. 1. Temperature dependence of the phosphorescence lifetime. (a) Tris(bipyridine)ruthenium(II) cation in 4:1 (v/v) EtOH/MeOH matrix [4]. (b) $[Pt(pop)_4]^{4-}$ in 2:1 (v/v) ethylene glycol/water. The sublevel rate constants and the splitting parameters are given [5].



$$\tau = \frac{1 + \exp(-\varepsilon_1 / kT) + \exp(-\varepsilon_2 / kT)}{k_1 + k_2 \exp(-\varepsilon_1 / kT) + k_3 \exp(-\varepsilon_2 / kT)}$$

Fig. 2. Definition of rate constants and splitting parameters for a triplet manifold. For a two-level manifold the expression for τ is truncated. Fitting data to this equation is appropriate only for manifolds that remain in Boltzmann equilibrium throughout the decay process and for T-independent individual rate constants.

decay time of the phosphorescence plotted against the square of the B-field for $Re(I)Cl(CO)_3bpy$ is shown in Fig. 3 [9].

2.1.3. $^3d\sigma^*p\sigma$ emission

The binuclear complex $[Pt_2(pop)_4]^{4-}$ ($pop = \mu\text{-}H_2P_2O_5$) has been extensively studied [5,10–13]. The phosphorescence has been assigned to a triplet manifold that

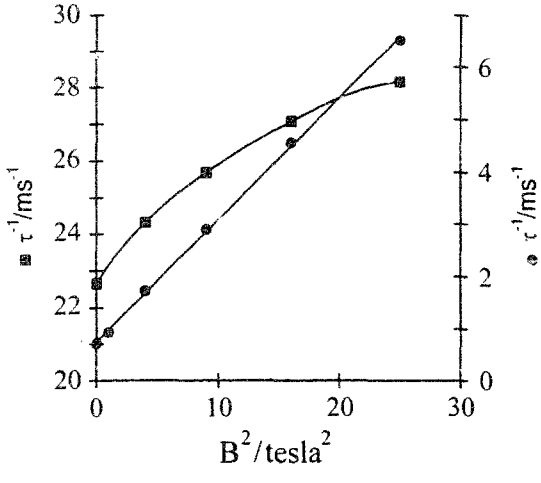


Fig. 3. Dependence of the phosphorescence lifetime on an applied magnetic field. ● [Right ordinate] $Pt(CN)_2(\mu\text{-diphenylphosphinomethane})_2$ at 4 K [8]. ■ [Left ordinate] $Re(I)Cl(CO)_3(bpy)$ at 2.2 K [9].

is composed of two levels, a single forbidden one lying lower and a second partially allowed level lying ca. 50 cm^{-1} higher in energy. For complexes with D_4 or higher symmetry about the internuclear axis group, theoretical arguments assign the lower level to a dipole-forbidden state and the upper level to a degenerate pair that arises from the triplet term but is made partially allowed by configurational mixing with upper singlet states [5,12]. The *T*-dependence of the phosphorescence decay time below 77 K confirms these assignments. This pronounced temperature dependence, shown in Fig. 1, is accurately reproduced by a two-level manifold that is obtained by truncating the expression shown in Fig. 2 to two levels. Indeed, one can employ the converse: a *T*-dependence curve of the phosphorescence decay time that can be fit adequately by a two-level model is strong evidence for axial orbital symmetry of the emitting triplet term. We have applied this argument to rationalize the data of a host of Rh(I), Ir(I), and Pt(II) binuclear complexes [8]. We conclude that within the precision of the measurements the orbital symmetry of the lowest (emitting) triplet term is axial, although the molecular symmetry ranges from D_{4h} to (pseudo)C_{2v}. The rate constants k_1, k_2 and the splitting parameter ϵ_1 for representative binuclear complexes are reproduced in Table 1. A dependence on the nature of the metal ions is evident.

The effect of a magnetic field on the phosphorescence decay time of a typical binuclear complex displaying $^3d\sigma^*p\sigma$ emission is also shown in Fig. 3. A linear relationship between the rate of decay ($1/\tau$) and the square of the magnetic field exists. This linearity is expected from the application of second-order perturbation theory to a two-level system with widely different decay constants [14,15]. Indeed, we infer that the occurrence of a linear relationship of this type is indicative of a two-level manifold essentially isolated from other excited manifolds in the complex. The behavior of the phosphorescence decay time in the external field confirms the presence of a two-level manifold and hence the existence of essentially axial electronic symmetry in complexes possessing lower than axial molecular symmetry.

As the two previous examples show, the behavior of the phosphorescence decay time (4 K) with magnetic field differs for ^{3}MLCT and $^3d\sigma^*p\sigma$ emitting manifolds. Thus, the magnetic field dependence of the phosphorescence decay time at very low

Table 1
Experimental parameters for the emitting triplet manifolds of platinum(II) complexes

Complex	Matrix	ϵ (cm^{-1})	k_1 (μs^{-1})	k_2 (μs^{-1})
$[Pt(CN)_2Rh(I)(t\text{-}BuNC)_2(\mu\text{-}dppm)_2][PF_6]$	PMMA	14	0.00078	0.13
$[Au(I)Pt(CN)_2(\mu\text{-}dppm)_2][PF_6]$	PMMA	61	0.0022	2.30
$Pt(CN)_4(\mu\text{-}dppm)_2$	PMAA	67	0.00064	2.62
$K_4[Pt_2(pop)_4]$	glycol water	50	0.0011	0.63
$Pt(bpy)(CN)_2$	solid	30	0.00048	2.1
$Pt(bpy)Cl_2$	solid	56	0.0034	4.0
$Pt(2\text{-}phpy)_2$	solid	41	0.0020	2.3
Pt(dpphen)(ecda)	DMM	50	0.006	2.2
Pt(dmbpy)(ecda)	DMM	52	0.013	2.0

temperatures becomes a criterion for distinguishing these two types of configurations in d^8 metal systems.

3. Investigations of the excited states of Pt(II) α,α′-diimine and orthometallated complexes

Assignment of the lowest excited electronic manifolds of Pt(II) complexes presents special difficulties. Unlike octahedral d^6 complexes [Ru(II), Re(I)], these d^8 species are square-planar, possessing open coordination sites at the metal ion. These sites facilitate solvent interactions in fluid solution, and they also promote aggregation of the species in solution and the formation of solids having linear chains of metal ions [16–18]. Following the pioneering work of Gliemann and coworkers [19], investigators have assigned the emission from the solids to a ^{3}MLCT manifold [20–22]. For complexes that exhibit emission in fluid solution, a ^{3}MLCT assignment has also been proposed [23]. The intriguing characteristics of these Pt(II) complexes have prompted us to reinvestigate their luminescence properties and to apply the additional criteria of *T*-dependence of the phosphorescence lifetime and the response of the decay time to magnetic perturbations to the experimental assignment of the lowest emitting manifolds.

3.1. Syntheses

Pt(bpy)$(CN)_2$, Pt(2-phpy)$_2$, and the red form of Pt(bpy)Cl_2 (bpy = 2,2′-bipyridine, 2-phpy = 2-phenylpyridine) were synthesized by published methods. The complex Pt(bpy)$(CN)_2$ was synthesized by Method A reported by Che et al. [24]. The procedure described by Morgan and Burstall [25] was followed to make the yellow form of Pt(bpy)Cl_2, which was subsequently converted to the red form by recrystallization from hot pyridine [26]. The orthometallated complex Pt(2-phpy)$_2$ was synthesized according to the procedure published by Chassot et al. [27]. Its structure was confirmed by X-ray powder diffraction. Pt(dpphen)(ecda) and Pt(dmpy)(ecda) (dpphen = 4,7-diphenyl-1,10-phenanthroline; ecda = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate; dmbpy = 4,4′-dimethyl-2,2′-bipyridine) were synthesized by the methods reported by Eisenberg and coworkers [28].

3.2. Spectroscopic measurements

3.2.1. T-dependence of the phosphorescence decay time

The 337 nm light from a Molectron UV-22 N_2 laser pulsed at 15 Hz (25 ns FWHM) was focused on an optical fiber that carried the light to the sample mounted inside a liquid He storage dewar. Temperature was monitored with a RuO_2 cryoresistor calibrated against an iron–rhodium secondary standard. The accuracy of the reported temperature values is ±3%. The emitted light from the sample returned through the same fiber, passed through a saturated aqueous KNO_2 solution, was

dispersed by a Spex Minimate monochromator, and detected by a RCA 31034 PMT. Signals were recorded on a LeCroy 9361 digital oscilloscope.

3.2.2. Magnetic field dependence measurements

To determine the effect of a magnetic field on the phosphorescence lifetime at 4 K, the samples were mounted in the cavity of a Janis Research super varitemp optical magnetic cryostat with the optical chamber flooded with liquid helium. The field strength was determined from the current measured in the coils. The excitation beam was oriented perpendicular to the *B*-field.

3.3. Results

3.3.1. Pt(bpy)(CN)$_2$, Pt(2-phpy)$_2$, and the red form of Pt(bpy)Cl$_2$

The experimental results from the *T*-dependence measurements on the phosphorescence for each substance were adequately fit by the two-level model described above. The data for Pt(bpy)(CN)$_2$ are shown in Fig. 4. The resultant decay constants and splitting parameters are listed in Table 1. The magnetic field dependence of the phosphorescence lifetime was measured for both Pt(bpy)(CN)$_2$ and Pt(2-phpy)$_2$ and a linear dependence of the decay rate on the square of the *B*-field was found. The plot for the orthometallated species is reproduced in Fig. 5.

3.3.2. Pt(dmbpy)(ecda) and Pt(dpphen)(ecda)

Depending on the solvent composition, in rigid glasses these complexes emit a high-energy and a low-energy band. Here we focus on the low-energy band that appears both in the rigid state and in fluid solution. The *T*-dependences of the phosphorescences for these substances in frozen DMM glasses [DMM = 1,1,1 (v/v) DMF, CH_2Cl_2, CH_3OH] were measured in the 77–4 K range. The results for Pt(dpphen)(ecda) are reproduced below in Fig. 6. A two-level model fits the data well. The resultant manifold parameters for both ecda species are given in Table 1.

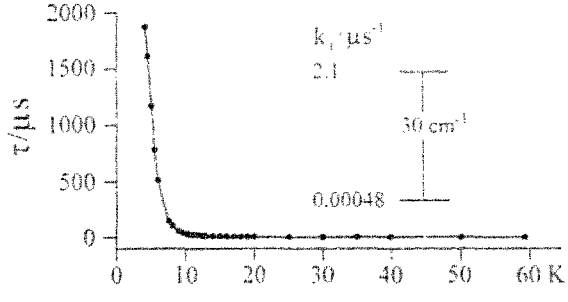


Fig. 4. Temperature dependence of the low-energy (red) phosphorescence of Pt(bpy)(CN)$_2$. · · · Experimental points. ——— computer-generated best fit. Derived rate constants and splitting parameter are included in the diagram and in Table 1.

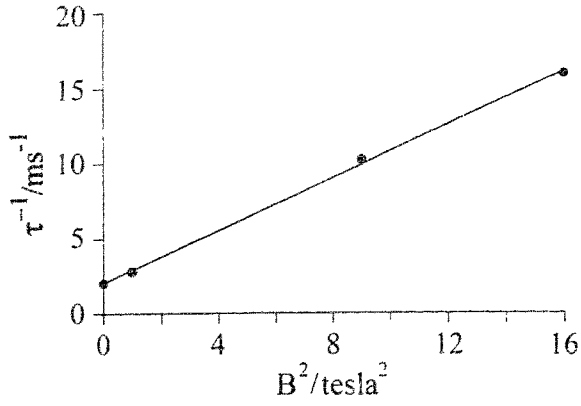


Fig. 5. Response of the phosphorescence decay time of Pt(2-phpy)$_2$ to an external magnetic field applied at 4.2 K.

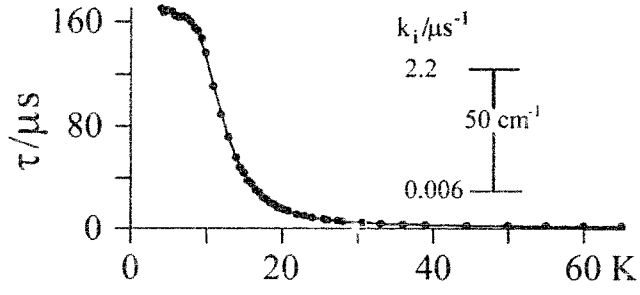


Fig. 6. Temperature dependence of the phosphorescence lifetime of Pt(dpphen)(ecda). · · · Experimental points. ——— computer-generated best fit. Derived rate constants and splitting parameter are included in the diagram and in Table 1.

4. Discussion

Although the spectral characteristics and the decay time at 77 K are indicative of the nature of the excited configuration responsible for the phosphorescence exhibited by a metal complex, these experimental data are insufficient to make a definitive assignment of the manifold for all substances. We assert, however, that the additional information provided by the *T*-dependence of the phosphorescence allows a unique assignment in most cases. When complemented by the behavior of the phosphorescence decay time at 4 K in a magnetic field, the assignment is secure.

Pt(bpy)(CN)$_2$, Pt(2-phpy)$_2$, and the red form of Pt(bpy)Cl$_2$ were studied in the solid state. Pt(2-phpy)$_2$ forms discrete dimers in the solid [27], but the other two crystallize with extended chains of Pt(II) atoms oriented along the unique axis of the crystal [18,29]. Each crystalline material contains Pt ions separated by ca. 3.4 Å. All three substances emit light in the red region of the spectrum and the bands display no discernible structure. Each phosphorescence decays with an approximately microsecond lifetime at 77 K, and each displays a *T*-dependence of the decay time

that can be adequately fit with a two-level scheme. The relevant data and the resultant parameters for the emitting manifold are given in Table 1. From these results we infer that the postulated model for the $[Pt_2(pop)_4]^{4-}$ ion is applicable to these materials also. This model is reproduced in Fig. 7. In this scheme there is no formal Pt–Pt bond in the ground state, but a transient bond is formed in the excited configuration. To a good approximation the electronic symmetry is axial in the lowest triplet manifold. In the $D_{\infty h}$ group the upper level is formally dipole-allowed with the *E*-vector perpendicular to the Pt–Pt axis and the lower state is strictly dipole forbidden.

For the $Pt(2\text{-phpy})_2$ solid that contains isolated dimers, no additional discussion is required. For the extended solids, however, the fit of the data to a dimer model requires further comment. In our view excitation of the solid is essentially to a singlet excitonic state as described by Gliemann and coworkers [19]. Rapid radiationless decay to triplet exciton(s) occurs, but the exciton becomes self-trapped, essentially forming an isolated excited dimer defect in the crystal. The latter is responsible for the observed phosphorescence and thus the emission resembles that of a discrete binuclear Pt(II) species.

Pt(II)(dmbpy)(ecda) and Pt(II)(dpphen)(ecda) are luminescent in fluid solution. The red emission shifts further red as the solution is cooled and retains its integrity in the glass [2,23]. The phosphorescence decay is clearly amenable to a two-level fit of the data. Indeed, the rate constants and the splitting of the two levels (Table 1) are remarkably similar to those observed for Pt(II) dimers and the extended chains investigated here and to the parameters of $[Pt_2(pop)_4]^{4-}$ that are also included in Table 1. From these data we conclude that the red emission observed from these Pt(II) species also originates from a $^3d\sigma^*p\sigma$ term. In our view these species aggregate

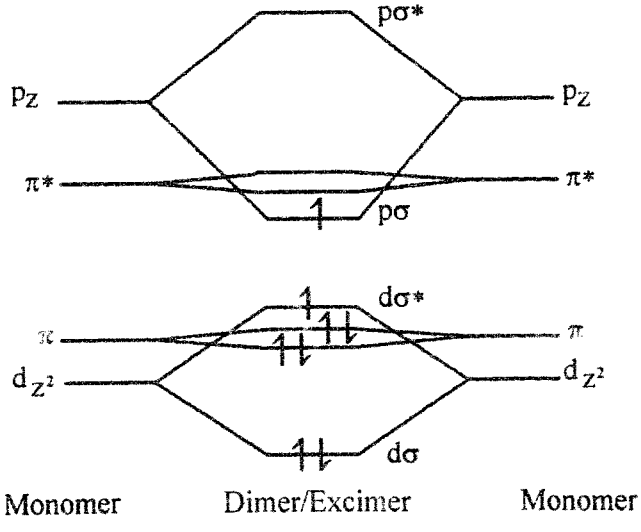


Fig. 7. Schematic orbital diagram for an excited triplet term of a d^8–d^8 binuclear complex. The diagram is also applicable to a trapped triplet exciton in crystals containing linear chains and aggregates in solutions and glasses.

in the glass and the emission arises principally from these aggregates. Thus, the behavior of these species is also adequately rationalized by the scheme portrayed above for the solids containing extended chains of Pt(II) ions. This view of the emission origin differs from that promulgated by Eisenberg and coworkers [23].

5. Summary

We have reinvestigated the prominent phosphorescence from several Pt(II) species, both in glasses and in solids. In all cases the red phosphorescence is attributed to an excited $^3d\sigma^*p\sigma$ manifold with essentially axial electronic symmetry about the Pt(II)–Pt(II) axis. Our reassignment of the origin of this red phosphorescence is dictated by the additional information obtained from the *T*-dependences of the decay times and the responses of the decay times to an external magnetic field. Our magnetic data agree with the previous work of Gliemann and coworkers [19]; however, our interpretation differs because of the additional information available from analogous measurements on discrete binuclear Pt(II) species [8]. Detailed information on the lowest emitting manifolds of these Pt(II) complexes and solids will be published elsewhere.

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