Coordination Chemistry Reviews
171 (1998) 85–92

Luminescent excimers and exciplexes of $\mathrm{Pt^{II}}$ compounds

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Received 7 July 1997; received in revised form 22 September 1997; accepted 19 November 1997

Contents

Abstract 85
1. Introduction 85
2. Experimental 86
3. Results and discussion 86
    3.1. Excimer of $\mathrm{Pt(bphen)(CN)_2}$ 86
    3.2. Exciplex of $\mathrm{Pt_2(P_2O_5H_2)_4^{4-}}$ with $\mathrm{Au(CN)_2^-}$ 90
4. Conclusions 91
Acknowledgements 92
References 92

Abstract

Spectroscopic and lifetime studies of luminescent excimer formation involving the lowest triplet excited state of $\mathrm{Pt(4,7\text{-}diphenyl\text{-}1,10\text{-}phenanthroline)(CN)_2}$ in dichloromethane solutions at room temperature are reported. Such experiments yield information related to the rate constants characterizing excimeric formation and decay. The $\mathrm{Pt^{II}}$ dimer $\mathrm{Pt_2(P_2O_5H_2)_4^{4-}}$ together with $\mathrm{Au(CN)_2^-}$ in deoxygenated aqueous solution exhibits a low energy luminescence band. An exciplex resulting from direct $\mathrm{Pt^{II}}$–$\mathrm{Au^{I}}$ interactions between these ions is postulated to be responsible for the observed luminescence. This appears to be the first exciplex reported between square planar d^8 and linear d^{10} ions, as well as the first between like-charged ions.
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Keywords: Exciplex; Excimer; Luminescence; Metal-metal bonding; Relativistic effects

1. Introduction

A steadily increasing number and variety of exciplexes and excimers of coordination compounds have now been reported [1,2]. Among these, coordination com-

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PII S0010-8545(98)00037-X

pounds of Pt^{II} show a tendency to form luminescent excimers [3–6] and exciplexes [2] in fluid solution at room temperature. We report here the results of quantitative studies of a previously reported excimer of $Pt(bphen)(CN)_2$ (bphen = 4,7-diphenyl-1,10-phenanthroline) [3]. We also report the formation of a new luminescent exciplex from $Pt_2(P_2O_5H_2)_4^{4-*}$ and $Au(CN)_2^-$ in aqueous solution, presumably a consequence of direct Pt^{II}–Au^{I} interactions.

The ability of coordinatively unsaturated compounds of d^8 and d^{10} *d*-block metals to experience attractive metal–metal interactions is becoming increasingly well-recognized [7]. These interactions are among the strongest ones observed for closed-shell molecules [8]. We have taken advantage of the fact that light can "crack open" such closed-shell metals and lead to enhanced metal–metal interactions in forming luminescent exciplexes [2]. For example, $Pt_2(P_2O_5H_2)_4^{4-}$ forms luminescent exciplexes with Tl^+ ions in aqueous solution [2]. We have extended these studies to include $Au(CN)_2^-$ which, like Tl^+, results in the formation of a lower energy luminescence band in deoxygenated aqueous solutions of this Pt^{II} dimer. This appears to be the first report of a luminescent exciplex formed between square planar d^8 and linear d^{10} ions, as well as the first between like-charged ions in solution.

2. Experimental

The compounds $Pt(bphen)(CN)_2$ and $K_4[Pt_2(P_2O_5H_2)_4]\cdot{}_2H_2O$ were prepared as described previously (refs. [3] and [2], respectively). $K[Au(CN)_2]\cdot 2H_2O$ (Atomergic, 99.9%) was recrystallized from water. All solvents were of spectroscopic or HPLC grade and were used as received. Corrected emission spectra were obtained with a Spex 1680 0.22 m double monochromator luminescence spectrometer interfaced to an IBM-PC computer. A 450 W xenon lamp, slit widths of 1 or 2 mm, and an integration time of 1 s were used in all cases. Luminescence quantum yields were obtained relative to quinine sulfate [9,10]. Luminescence lifetimes were obtained from analysis of monoexponential decay curves produced from excitation of Ar-degassed samples with 337 nm light from an LSI pulsed nitrogen laser and detected with a photomultiplier tube connected to a LeCroy digital oscilloscope.

3. Results and discussion

3.1. Excimer of $Pt(bphen)(CN)_2$

The corrected luminescence spectra (excitation at 360 nm) of dichloromethane solutions of $Pt(bphen)(CN)_2$ at two different concentrations are shown in Fig. 1.

At low concentrations of $Pt(bphen)(CN)_2$ [Fig. 1(b)] there is a relatively structured high-energy luminescence centered near 525 nm (19 000 cm^{-1}) and assigned as before [3] to a bphen-localized π–π* excited state. The luminescence spectrum was resolved by curve fitting procedures into three component Gaussian bands equally spaced about 1130 cm^{-1} apart. The luminescence decreases in intensity as

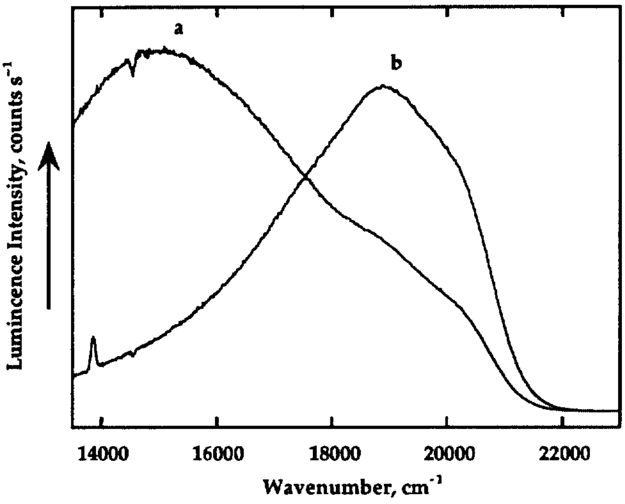


Fig. 1. Corrected luminescence spectra of Pt(bphen)(CN)$_2$ in deoxygenated CH_2Cl_2 at (a) 1.7×10^{-4} mol l^{-1} and (b) 9.0×10^{-6} mol l^{-1}.

the concentration increases, and a broad, unstructured low-energy luminescence near 665 nm (15 000 cm^{-1}) attributed to the excimer of Pt(bphen)(CN)$_2$ becomes increasingly prominent at higher concentrations [Fig. 1(a)]. Fig. 2 provides an example of how an emission spectrum at intermediate concentration can be resolved into three overlapping excited state monomer bands and a single excimer band. Integration of these component bands then yields the relative intensities of the luminescence attrib-

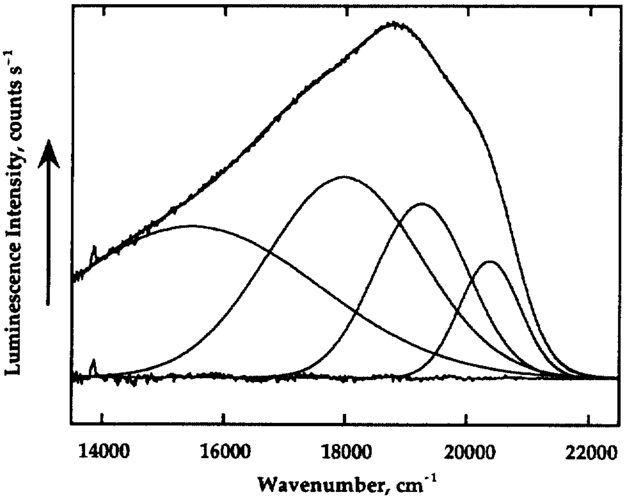


Fig. 2. Component Gaussian bands of the luminescence spectrum of Pt(bphen)(CN)$_2$ in deoxygenated CH_2Cl_2 at 4.5×10^{-5} mol l^{-1}.

uted to the monomer and dimer (excimer) excited state species. A plot of this ratio as a function of concentration (Fig. 3) reveals the predicted linear relationship [2] with slope $(2.69 \pm 0.06) \times 10^4\ \mathrm{l\ mol^{-1}}$. This slope is a crude measure of the equilibrium constant for excimer formation.

The luminescence decays of $\mathrm{Pt(bphen)(CN)_2}$, produced by excitation at 337 nm with a pulsed nitrogen laser, were observed to be monoexponential under the present conditions. The reciprocal of the lifetimes obtained are shown in Fig. 4 as a function of concentration. The lifetime decreases sharply with increasing concentration from the extrapolated limit of 130 ± 10 μs at zero concentration. A plot of lifetime versus the reciprocal of concentration at the highest concentrations used (not shown) provides a rough estimate of $\tau_D \approx 3$ μs for the lifetime of the excimer. Such behavior is predicted by steady-state kinetic schemes assuming two luminescent species [1,11,12] (Scheme 1), the slope of the line in Fig. 4 ($5 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$) corresponding to the ratio $k_3(k_5+k_6)/k_4$.

Also, according to this scheme, the slope of the line in Fig. 3 ($3 \times 10^4\ \mathrm{l\ mol^{-1}}$) should correspond to the ratio $k_5k_3/[k_1(k_4+k_5+k_6)]$ and is very approximately related to the equilibrium constant for exciplex formation, k_3/k_4. The quantum yield for luminescence at low concentrations, $k_1/(k_1+k_2)$, was determined to be 0.090 ± 0.009. This value, in combination with the limiting lifetime value at low concentrations (130 μs), yields values of $6.9 \pm 1.1\ 10^2\ \mathrm{s^{-1}}$ and $6.9 \pm 0.6\ 10^3\ \mathrm{s^{-1}}$ for k_1 and k_2, respectively. The quantum yield and lifetime values are consistent with the values of 0.097 and 223 μs, respectively, reported recently for the related compound $\mathrm{Pt(5\text{-}Ph\text{-}phen)(CN)_2}$ in $\mathrm{CH_2Cl_2}$ [13]. More accurate lifetime measurements are needed at high concentrations if a reliable lower limit to the lifetime is to be established. Such data, along with the spectroscopic data, would enable estimates for the remaining rate constants to be made.

A central question concerning excimers formed from $\mathrm{Pt^{II}}$ compounds containing

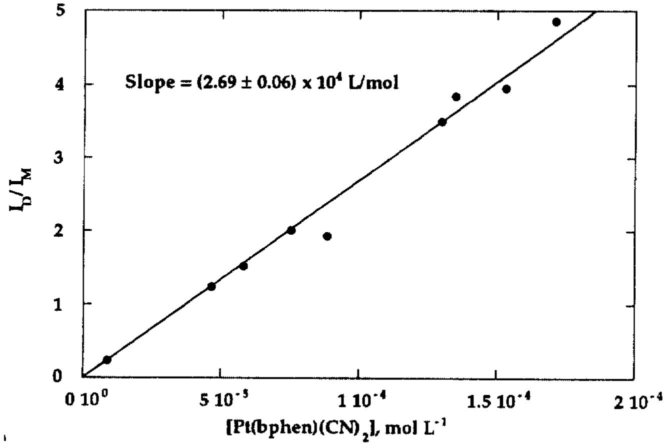


Fig. 3. Plot of the ratio of integrated luminescence intensities for the excimer (I_D) versus monomer (I_M) for $\mathrm{Pt(bphen)(CN)_2}$ as a function of concentration in deoxygenated $\mathrm{CH_2Cl_2}$.

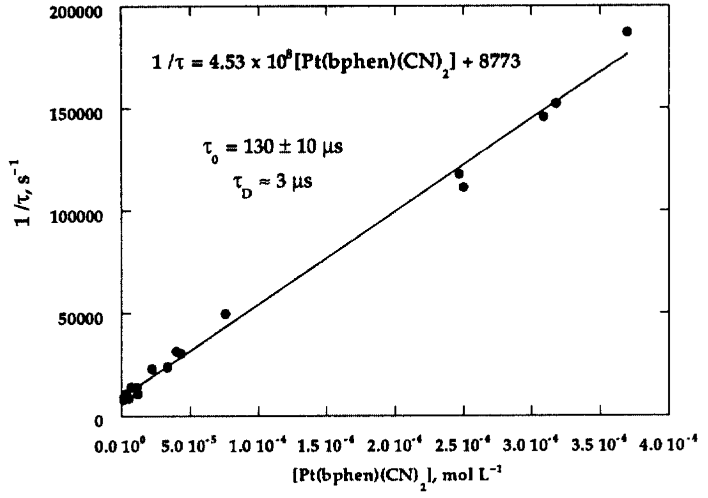
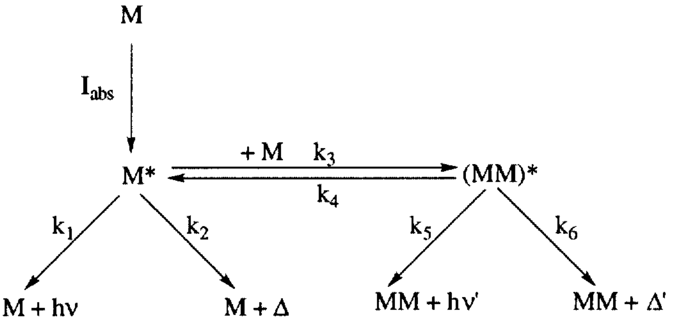


Fig. 4. Plot of the reciprocal of the luminescence lifetime of Pt(bphen)(CN)$_2$ as a function of concentration in deoxygenated CH$_2$Cl$_2$ solution. τ_0 represents the limiting value of the lifetime at zero concentration and τ_D is an estimate of the lifetime of the excimer obtained by extrapolation of a plot of τ versus reciprocal concentration.



Scheme 1.

polyimine ligands is the nature of the attractive interaction between the excited state and its ground state analogue. By analogy with compounds of general formula Pt(trpy)X$^+$, either Pt–Pt or bphen–bphen ring interactions (or both) could account for such attractive interactions. The various possible frontier orbital interactions involved in the low energy absorption and luminescence processes in both the solid state and solution have been considered [14–18]. All that can be said for Pt(5-Ph-phen)(CN)$_2$ is that the ground state HOMO is likely to be a σ^* orbital of either Pt–Pt d_{z^2}–d_{z^2} or bphen–bphen π–π parentage, and the LUMO is a σ orbital of either (or both) Pt–Pt p_z–p_z or bphen–bphen π^*–π^* parentage. Thus metal localized, ligand localized, and MLCT states are all possible candidates for the lowest energy absorption and emission bands of Pt(bphen)$(CN)_2$ and its excimer. Our data do not help to distinguish among these various possibilities.

3.2. Exciplex of $Pt_2(P_2O_5H_2)_4^{4-}$ with $Au(CN)_2^-$

We have observed luminescent exciplex formation between a square planar Pt^{II} and a linear Au^I coordination compound for mixtures of $Pt_2(P_2O_5H_2)_4^{4-}$ and $Au(CN)_2^-$ in aqueous solution (Fig. 5).

In addition to the usual $Pt_2(P_2O_5H_2)_4^{4-}$ fluorescence and phosphorescence bands at 400 and 514 nm (25 000 and 19 500 cm^{-1}), respectively, Gaussian resolution of the observed emission spectrum at 0.10 mol l^{-1} $Au(CN)_2^-$ (Fig. 6) reveals new luminescence bands centered at 440 and 571 nm (22 700 and 17 500 cm^{-1}). The band at 440 nm is presumably due to fluorescence from an excited $Pt_2(P_2O_5H_2)_4^{4-}$–$Au(CN)_2^-$ ground state ion pair. While there are no noticeable changes in the absorption spectrum of $Pt_2(P_2O_5H_2)_4^{4-}$ at this concentration, even otherwise insignificant absorbance originating from such an ion pair would account for the weak fluorescence at 440 nm. The 571 nm band is attributed to a phosphorescent exciplex of formula $[Pt_2(P_2O_5H_2)_4^{4-}$–$Au(CN)_2^-]$. By analogy to the exciplexes involving Tl^+ [2], this exciplex presumably involves direct Pt^{II}–Au^I interactions at one of the axial Pt–Pt sites.

Although only preliminary results have been obtained to date, the resemblance to the well-established exciplex luminescence of $Pt_2(P_2O_5H_2)_4^{4-}$ with Tl^+ is striking [2], the most notable difference being the much higher concentrations of $Au(CN)_2^-$ needed to form an exciplex. For example, large changes in the emission spectrum of $Pt_2(P_2O_5H_2)_4^{4-}$ are observed below Tl^+ concentrations of 10^{-5} mol l^{-1}, while such effects are only found above 10^{-2} mol l^{-1} for $Au(CN)_2^-$.

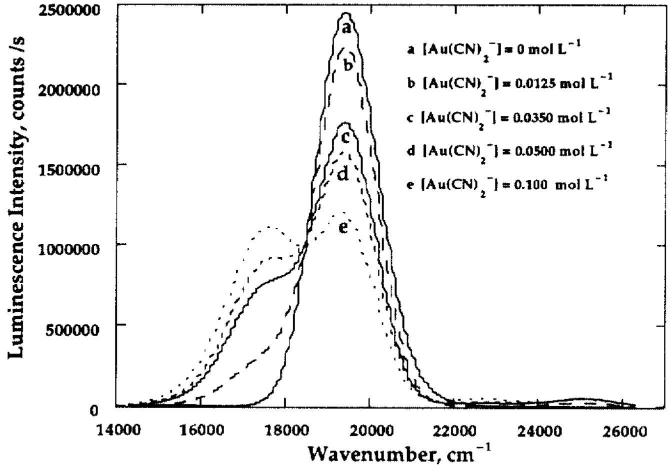


Fig. 5. Corrected emission spectra of deoxygenated aqueous solutions of 1×10^{-5} mol l^{-1} $Pt_2(P_2O_5H_2)_4^{4-}$ with various concentrations of $Au(CN)_2^-$.

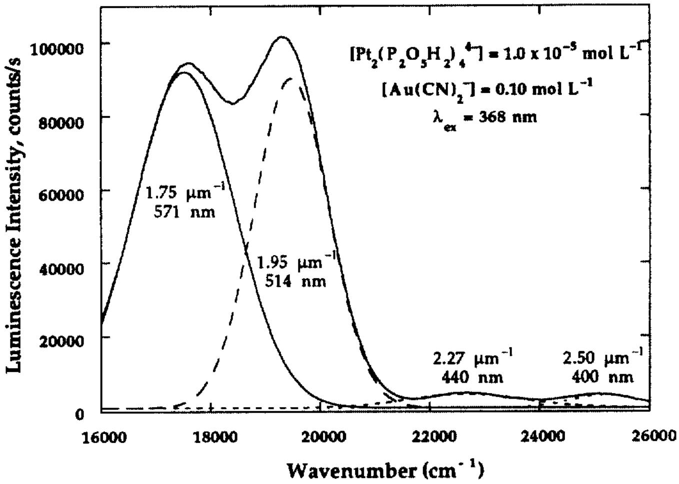


Fig. 6. Corrected emission spectrum of a solution of 1×10^{-5} mol l^{-1} $Pt_2(P_2O_5H_2)_4^{4-}$ in the presence of 0.1 mol l^{-1} $Au(CN)_2^-$ in deoxygenated water, along with the four resolved Gaussian band components.

This is reflected in a plot of the 571 nm to 514 nm integrated band intensities for the spectra shown in Fig. 5 (not shown; similar to the plot in Fig. 3) which yields a slope of 4.2 l mol^{-1}. This can be compared to the value of 1.2×10^5 l mol^{-1} for the analogous $Pt_2(P_2O_5H_2)_4^{4-}$–Tl^+ exciplex. Additional spectroscopic and lifetime measurements are being made to better characterize the $Pt_2(P_2O_5H_2)_4^{4-}$–$Au(CN)_2^-$ exciplex.

Since Hg is isoelectronic with Tl^+, the excited state dimer Hg_2^* can serve as a simple gas-phase model for such metal–metal bonded exciplexes. This excimer exhibits fluorescence at 335 nm and has been proposed as a candidate for an excimeric laser [19,20]. Similarly, Hg_2 can serve as a simple model for understanding the nature of the attractive forces between such heavy metals in their closed shell electronic ground states. Although relativistic effects undoubtedly play a contributing role in such metal–metal interactions [8,21], correlation effects apparently play the dominant role in making these atoms "stick" to each other [8]. Parenthetically, Hg* also serves as a model [22] for the interesting atom abstraction reactions exhibited by the lowest triplet excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ [23].

4. Conclusions

Although direct, relativistically enhanced Pt^{II}–Au^I interactions are undoubtedly responsible for exciplex formation in aqueous solutions of $Pt_2(P_2O_5H_2)_4^{4-}$ with $Au(CN)_2^-$, excimer formation in CH_2Cl_2 solutions of $Pt(bphen)(CN)_2$ most likely results from either (or both) π–π interactions of the phenanthroline ligands or direct Pt–Pt orbital overlap [14]. This illustrates the difficulty in making generalizations about the nature of excited state interactions of square planar compounds of Pt^{II}.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the ACS, for support of this work. JKN thanks the Fulbright Foundation for a Fulbright Scholar award, Bowdoin College for sabbatical leave support, and Dr. Julia Weinstein for helpful discussions.

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