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SOLVATOCHROMIC AND EMISSIVE PROPERTIES OF Pt(II) COMPLEXES WITH 1,1- AND 1,2-DITHIOLATES

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Abstract: A series of Pt(L-L)(S-S) complexes is studied where (N-N) is an α,α'-diimine, a diamine or a chelating phosphine ligand and (S-S) is either a dithiolate chelate or bis(thiolate) ligands. All of the diimine complexes show an intense solvatochromic band in the 400-500 nm region of the spectrum which shifts to higher energy with increasing solvent polarity whereas the absorption of the diamine and phosphine complexes is insensitive to solvent. The emission behavior of these complexes at low temperature depends on the (S-S) ligand. When (S-S) is maleonitriledithiolate (mnt), the emission in rigid glass is structured and shows single exponential behavior with both emission lifetime and intensity increasing with decreasing temperature. For the other Pt(diimine)(S-S) studied, the temperature dependence of the emission lifetime and quantum yield provide evidence of multiple emitting states. Complexes which contain a saturated diamine, diphosphine or bis(phosphine) ligands and show no solvatochromism, exhibit emission consistent with a single emitting state. Based on the spectroscopic data, the lowest energy absorption in the diimine complexes is assigned as a metal-dithiolate to diimine charge transfer transition. In diamine and phosphine complexes the absorption is assigned as a metal-to-dithiolate MLCT transition. For all the diimine complexes except those of mnt, the emission is assigned as $^3(\mathrm{Pt(d)/S(p)} - \pi^*_{\mathrm{diimine}})$ while for the mnt complexes, the emission corresponds to $^3(\mathrm{Pt(d)/S(p)} - \pi^*_{\mathrm{mnt}})$. Comparison of the spectroscopic results with extended Hückel molecular orbital calculations support these assignments.

INTRODUCTION

The photochemical and photophysical properties of a molecule depend on the orbital nature of its lowest excited state and the proximity of other excited states. It is therefore

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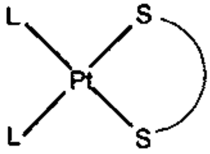
essential in the development of transition metal photochemistry to elucidate the nature of electronic excited states of metal complexes through photophysical methods and systematic variation of the donor and acceptor properties of the ligands. Significant efforts have been made in this direction during the past 20 years, particularly with octahedral d^6 complexes having heteroaromatic chelating ligands.[1] Interest in luminescent d^8 square planar complexes has increased significantly in recent years and a number of examples have been reported.[2-9] Particularly notable are the recent reports of square planar Pt(II) complexes which emit in fluid solution such as the cyclometallated system $Pt(thpy)_2$ (thpy = 2,2'-thienylpyridine) and analogous orthometallated complexes containing the ligands phenylpyridine (phpy), benzo[h]quinoline (bhq) and phenylpyrazole (phpz) first reported by Balzani, von Zelewski and coworkers,[8,9] and the Pt(diimine)(dithiolate) complexes described here.[6,7]

Of special interest are square planar complexes containing two different unsaturated chelating ligands, one that can be more easily reduced and the other one more easily oxidized. Examples of this class are square planar complexes containing an α,α'-diimine and an unsaturated dithiolate. Systems of this type were first examined by Dance and later studied by Vogler and include complexes of Ni(II), Pd(II) and Pt(II.)[10-12] These systems exhibit an intense solvatochromic absorption band which was assigned to an *inter*ligand π–π^* charge transfer (LLCT) from the dithiolate to the diimine ligand. Low temperature luminescence studies were performed on these systems by Vogler.[11] Related pseudo-tetrahedral d^{10} Zn and Cd complexes containing an α,α'-diimine and bis(thiolate) ligands were studied in detail by Crosby[13] both in rigid glasses and in the solid state. For both the d^8 square planar complexes and the d^{10} pseudo-tetrahedral systems the emission was assumed to arise from the same excited state as the solvatochromic absorption.

We previously described a series of Pt(diimine)(dithiolate) complexes which show strong solvatochromism in their absorption spectra and exhibit the remarkable property of being luminescent in fluid solution.[6,7] While the solvatochromic absorption seems to be a common feature of all of the Pt(diimine)(dithiolate) complexes, the emission behavior of these systems shows marked differences depending on whether (S-S) is a 1,1- or a 1,2- dithiolate. Based on these results, the solvent dependent absorption was tentatively assigned to be MLCT or LLCT in nature and the emission to arise from a MLCT d-π* state involving the dithiolate ligand. We describe here a more extensive study of these complexes through photophysical measurements and systematic ligand variation. The results are supported by extended Hückel molecular orbital calculations.

RESULTS AND DISCUSSION

The complexes described here are prepared by reaction of the PtL_2Cl_2 complex with an excess of the sodium or potassium salt of the dithiolate in MeOH. The complete synthesis and characterization of the complexes have been described elsewhere.[14,15]

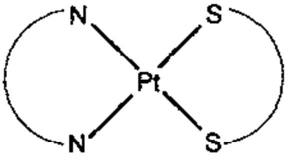


L, L' = dmbpy, dpphen, t-dach, $(PR_3)_2$, $(P(OR)_3)_2$, $R_2PCH_2CH_2PR_2$

S-S = mnt, ecda, edt, $(EtS)_2$, $(PhS)_2$, $(PhSe)_2$

dmbpy = 4,4'-dimethyl-2,2'bipyridine
dpphen =4,7-diphenyl-1,10-phenanthroline
t-dach = (±) *trans*-diaminocyclohexane
mnt = maleonitriledithiolate = 1,2-dicyano-1,2-ethylenedithiolate
ecda = ethyl-2-cyano-3,3-di(thiolato)acrylate
edt = 1,2-ethanedithiolate
EtS = ethylthiolate
PhS = phenylthiolate
PhSe = phenylselenolate

The electronic absorption spectra of the complexes containing a diimine ligand differ markedly from those containing a saturated diamine, di(phosphine) or bis(phosphine) ligands. All of the diimine complexes (containing an unsaturated or saturated dithiolate or bis(thiolate) ligands) show a very intense absorption band in the 450-600 nm region of the spectrum ($\varepsilon > 10,000$) whose energy increases with increasing solvent polarity. In contrast, the complexes containing diamine or phosphine ligands possess only a weak shoulder in the visible portion of the spectrum that is independent of the polarity of the solvent. The basis of solvatochromism has been probed by systematic ligand variation in the complexes shown as I-VI. It is observed



Compound	N-N	S-S
Ia	dmbpy	mnt
Ib	dpphen	mnt
IIa	dmbpy	ecda
IIb	dpphen	ecda
IIIa	t-dach	mnt
IIIb	t-dach	ecda
IVa	dmbpy	edt
IVb	dpphen	edt
Va	dmbpy	$(EtS)_2$
Vb	dpphen	$(EtS)_2$
V	dmbpy	$(PhS)_2$
VI	dmbpy	$(EtSe)_2$

that the intense solvatochromic transition only ocurs in complexes containing an unsaturated diimine ligand and S (or Se) donor atoms. This indicates that the solvatochromic transition is from a filled orbital having significant sulfur p character to an unocccupied level which is a π^*diimine orbital. This assignment, which is modified slightly below based on molecular orbital calculations and photophysical studies, is in essential agreement with that of Dance[10] and Vogler[11] as a LLCT transition.

All of the unsaturated dithiolate complexes studied luminesce in the solid state and in rigid glasses at 77 K. There are, however, striking differences between the emission of complexes which contain the 1,2-dithiolate mnt and those containing the 1,1-dithiolate ecda. Emission spectra from mnt complexes are highly structured with a main vibrational progression of ~1400 cm^{-1}. The energies and structure of the emission are remarkably similar to those reported previously by Johnson, *et al.*, for MLL'(mnt) complexes (M = Rh, Ir; L, L' = PR_3, $P(OR)_3$, CO)[4] which have been assigned as a $^3(d - \pi^*_{mnt})$ MLCT transition. This assignment was made based on the similarity of the structured emission for all the complexes studied and the observed decrease in emission energy with increasing donor ability of L and L'. In marked contrast, the emissions of ecda complexes are broad and show no structure even at temperatures as low as 6 K. This difference holds for all of the mnt and ecda complexes tested and is illustrated in Figure 1 for Pt(dppe)(mnt) and Pt(dppe)(ecda).

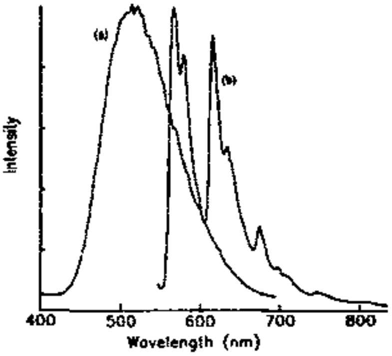


Figure 1. Emission spectrum of (a) $Pt(P(OPh)_3)_2$(mnt) and (b) $Pt(P(O\text{-}i\text{-}Pr)_3)_2$(ecda) at 77 K.

A remarkable property of the diimine complexes is the fact that they exhibit emission in fluid solution. These systems have been most extensively investigated as to the nature of their emitting state. The solution emission is broad and asymmetric and is centered at 600-650 nm.

Unlike the solvent dependent absorption bands, the emission energy is virtually independent of solvent polarity. However, the relative emission intensity decreases with increasing solvent polarity.

The temperature dependence of the emission in rigid glasses also differs significantly between the mnt and ecda complexes. For mnt complexes the emission energy does not change upon going from fluid solution to rigid glass. Between 165 K (the glassing temperature of the solvent mixture) and 6 K there is an increase in emission intensity with decreasing temperature accompanied by sharpening of the vibrational structure. The emission lifetimes show good first order decay. These results indicate that the emission originates from a single excited state.

The emission spectra of the ecda complexes Pt(dmbpy)(ecda) and Pt(dpphen)(ecda) have been studied as a function of temperature in DMF/CH_2Cl_2/MeOH (DMM) solution and frozen glass, and their emission quantum yields have been determined between 50 and 6 K using $Ru(bpy)_3Cl_2$ in EtOH glass as a standard.[16] The emission intensity of these complexes increases with decreasing temperature between 298 and ~175 K, while the emission energy and band shape remain constant. Between 175 K and 165 K a sharp shift of 1540 cm^{-1} to lower energy is observed as seen in Figure 2 for Pt(dpphen)(ecda). For all of these complexes, new bands A and B emerge in the emission spectra below 140 K. These bands as well as band C increase in intensity with decreasing temperature down to 80 K. Lowering the temperature from 50 K to 6 K results in little change in the intensity of bands A and B while band C shows a large decrease in emission intensity accompanied by a slight shift to lower energy. This is illustrated in Figure 3 for Pt(dmbpy)(ecda).

Different excitation spectra are obtained for Pt(dmbpy)(ecda) and Pt(dpphen)(ecda) depending on the chosen λ_{em}. Collection at bands A or B yields a more structured excitation spectrum with a lowest energy peak at ~475 nm. In contrast, collection at band C yields a broad excitation spectrum extending further into the red. Selective excitation experiments show that

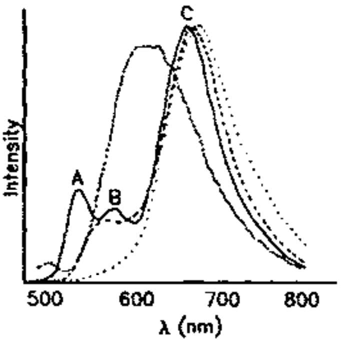


Figure 2. Emission spectrum of Pt(dpphen) in DMM glss at (---) 298 K, (· · ·) 165 K, (–-) 140 K and (—) 80 K.

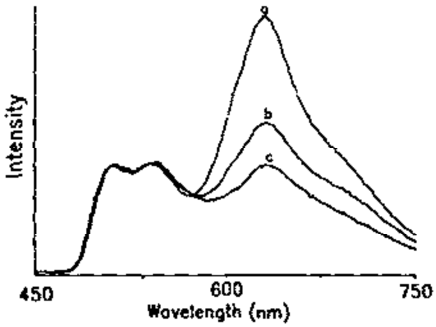


Figure 3. Emission spectrum of Pt(dmbpy)(ecda) in DMM glass at (a) 25 K, (b) 10 K, (c) 6 K.

all three bands are seen upon excitation at 442 nm but when λ_{exc} of 500 nm is employed, only band C is observed in the emission. The temperature dependence of the emission intensity of C is the same for the two different λ_{exc} studied, that is, the relative intensity and hence quantum yield for emission decrease as the temperature is lowered.

Lifetime studies show identical and relatively long lifetimes for bands A and B, supporting the notion that A and B result from a ligand based state and that the two bands correspond to vibronic components of the same excited state. These bands have previously been assigned to an intraligand (IL) $^3(\pi-\pi^*)$ diimine-based excited state by analogy with other well known phenanthroline- and bipyridine-containing complexes.[17-19] Band C, in contrast, exhibits a much shorter lifetime. For all three bands, the lifetime increases with decreasing temperature, as anticipated. The fact that the lifetime of band C gets longer as the temperature is lowered whereas the quantum yield for emission *decreases*, suggests that more than one excited state is responsible for the emission from band C. The excited state model employed in our analysis is similar to one developed by Crosby[16] for $Ru(bpy)_3^{2+}$ and is shown in Figure 4. The assumptions made for the derivation of the model as well as the expressions obtained for the lifetime and quantum yield have been published elsewhere.[15] An excellent fit was obtained from a non-linear least squares regression analysis of the model as shown in Figure 5. The values of the decay rate constants and energy separations for the two emitting states (for Pt(dmpby)(ecda): $k_{2r} = 6.16 \times 10^5\ s^{-1}$; $k_{3r} = 4.39\text{-}4.4 \times 10^5\ s^{-1}$; $\Delta E = 54.2\ cm^{-1}$; for Pt(dpphen)(ecda): $k_{2r} = 9.95 \times 10^5\ s^{-1}$; $k_{3r} = 1.28\text{-}4.4 \times 10^6\ s^{-1}$; $\Delta E = 52.5\ cm^{-1}$) are within the expected range for the radiative rate

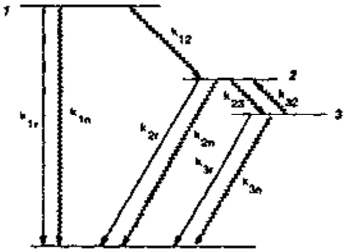


Figure 4. Excited state model for the emission of Pt(diimine)(ecda) complexes.

constants and splittings of spin-orbit terms for a third row d^8 metal center.[20] In contrast, the radiative rate constant k_r^{540} for bands A and B calculated from Φ_{540}/τ_{540} is 3.2×10^3 sec^{-1}, which is consistent with the assignment of A and B as a $^3(\pi-\pi^*)$ diimine based state.[21]

The Pt(diimine)(S-S) complexes where S-S is a saturated dithiolate chelate or bis(thiolate) ligands show remarkably similar properties to the ecda systems in their low temperature emission spectra, that is, their emission lifetime *increases* but their emission intensity *decreases* as the temperature is lowered from 50 to 6 K. These results suggest that the emission in these complexes also originates from more than one excited state. One notable difference is that the high energy emission from a π-π^* excited state is not seen for these complexes. A different emission behavior is observed for the Pt(ecda) complexes possessing an unsaturated diamine, di(phosphine) or bis(phosphine) ligands. These complexes exhibit an emission that is significantly blue shifted with respect to that of the diimine analogs and show an increase in both their excited state lifetime and emission quantum yield with decreasing temperature.

In order to probe the electronic nature of the solvatochromic transitions and the emissive states, extended Hückel molecular orbital calculations were performed using the MOAN and CACAO programs developed by Mealli and Proserpio.[22] A complete account of the results of the calculations has been published.[14] The results show that for all of the diimine dithiolate and bis(thiolate) complexes examined, the lowest unoccupied MO is almost exclusively π^*_{diimine}, whereas the highest occupied MO is a combination of Pt(d) and S(p) atomic orbitals as shown in Figure 5 for Pt(bpy)(mnt). The calculations thus indicate that the solvatochromic absorption is a Pt(d)/S(p) - π^*_{diimine} transition and that the emission is from a triplet state of the same orbital parentage. For the complexes containing saturated diamine or phosphine ligands, the nature of the HOMO changes very little from that of the diimine analogs, but the LUMO becomes

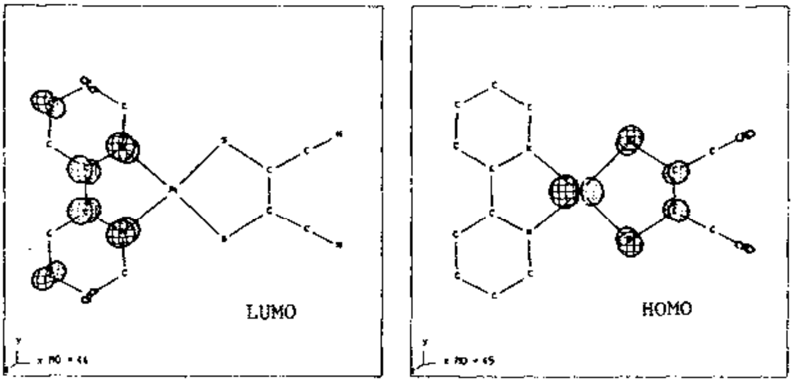


Figure 5. Molecular orbital representation for HOMO and LUMO of Pt(bpy)(mnt).

exclusively $\pi^*_{\text{dithiolate}}$ in character. This suggests that in the absence of π^*_{diimine} orbitals, the absorption and emission originate from a Pt(d)/S(p) - $\pi^*_{\text{dithiolate}}$ excited state, which is in agreement with the spectroscopic results. For the Pt(diimine)(mnt) complexes which show a structured emission of single exponential decay, a $\pi^*_{\text{dithiolate}}$ orbital lies in close proximity to the π^*_{diimine} LUMO while in Pt(mnt) complexes with saturated diamine and phosphine ligands the same $\pi^*_{\text{dithiolate}}$ orbital is the lowest unoccupied orbital. This low lying empty $\pi^*_{\text{dithiolate}}$ orbital identified by the calculations and the common structured emission for all mnt complexes leads to the assignment of the emission of all mnt complexes as a $^3(\text{d}-\pi^*_{\text{mnt}})$ MLCT transition.

CONCLUSIONS

Complexes of the type Pt(diimine)(dithiolate) exhibit both an intense solvatochromic absorption and emission which is observed at room temperature in fluid solution. The solvatochromic absorption is present in Pt(diimine) systems containing saturated dithiolates but disappears when the diimine is substituted by a saturated diamine chelate or by phosphine ligands. Based on systematic ligand substitution and molecular orbital calculations, the solvatochromic transition is in all cases ascribed to a (Pt(d)/S(p) - π^*_{diimine}) charge transfer. For all of the diimine complexes except those of mnt, the broad asymmetric emission is assigned as having the same orbital parentage as the solvatochromic absorption but arising from a state of different multiplicity. The temperature dependence of the emission intensity and excited state lifetimes of these systems indicate multiple state luminescence including emission from spin-orbit components of $^3(\mathrm{Pt(d)/S(p)} - \pi^*_{\mathrm{diimine}})$ and from $^3(\pi - \pi^*_{\mathrm{diimine}})$. All of the mnt complexes exhibit emissions having similar type and degree of structuring, leading to the conclusion that they possess a common emitting state. This state is assigned as $^3(\mathrm{Pt(d)}/S\mathrm{(p)} - \pi^*_{\mathrm{mnt}})$ based on systematic ligand variation and supported by MO calculations. For other unsaturated dithiolate complexes not having a diimine chelate, a similar emitting state of $^3(\mathrm{Pt(d)/S(p)} - \pi^*_{\mathrm{dithiolate}})$ is assigned.

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