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Electronic Spectra and Photophysics of Platinum(II) Complexes with α-Diimine Ligands. Solid-State Effects. 1. Monomers and Ligand π Dimers

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The absorption and emission spectra of four platinum(II) α-diimine complexes are compared in order to gain insight into the observed solid-state effects on emission behavior. In glassy solution, complexes with four coordinating nitrogen ligands exhibit emission from a diimine $^3(\pi-\pi^*)$ excited state. $Pt(bpy)Cl_2$, with a weaker ligand field, shows emission characteristic of a ^{3}(d–d) lowest excited state. In the solid state, $[Pt(bpy)(en)](ClO_4)_2$ and $Pt(bpy)Cl_2$ have nearly the same emission energies and band shapes as in solution, while $[Pt(bpy)_2](ClO_4)_2$ and $[Pt(phen)_2]Cl_2$ emission spectra show definite solid-state effects. These effects are ascribed to excimeric interaction between the diimine ligands of adjacent monomers in the unit cell and not to Pt–Pt electronic interaction.

Introduction

The electronic structures of square-planar Pt(II) complexes are often quite sensitive to solid-state effects. For example, in the original synthesis of $Pt(bpy)Cl_2$ (bpy = 2,2′-bipyridine),[1] Morgan and Burstall reported both a yellow form and a red form, which were later shown[2,3] to be different crystalline morphs of the same molecule. The yellow form contains essentially monomeric $Pt(bpy)Cl_2$, whereas the red form has a linear-chain structure with a Pt–Pt distance of 3.40 Å.[3] Many Pt(II) complexes crystallize in linear-chain stacks in which Pt–Pt interaction has been shown[4] to give rise to perturbed electronic absorption if the Pt–Pt spacing is sufficiently short. In some cases, such as Magnus' Green Salt ($[Pt(NH_3)_4][PtCl[4]]$), the color change due to this perturbation is striking. Other Pt(II) complexes, particularly double salts, are known to change color dramatically upon crystallization and/or dehydration,[5–7] and instances have been noted[8] of unusual differences between the emission spectra of some Pt complexes in glassy solution vs the microcrystalline solid. Recently, Chassot et al.[9] reported both solid-state absorption and strong emission in *cis*-bis(2-phenylpyridine)platinum(II) that have no counterpart in solution. The crystal structure of this complex[10] reveals a plane-parallel dimer packing with an interdimer distance of 3.37 Å and a Pt–Pt distance of 3.53 Å. Clearly, an electronic interaction between monomers can have a large effect upon the absorption and emission properties of Pt(II) complexes in the solid state. Perhaps the best documented example of this effect is that of linear-chain $Pt(CN)_4^{2-}$ salts, whose electronic spectra and photophysics are highly dependent upon the Pt–Pt spacing dictated by counterion and hydration number.[11]

During ongoing studies of the electronic structure and photophysics of Pt(II) dimeric complexes[12] and double-salt materials,[13] we have observed that the emission properties of Pt(II) complexes with coordinated diimine ligand(s) are often quite variable from the solution to the solid state. This variation could indicate solid-state Pt–Pt interaction, or it could be due to other effects such as ligand–ligand interaction. In order to gain insight into the relationship between crystal packing and electronic structure, we have focused on four representative diimine complexes, $Pt(bpy)(en)^{2+}$, $Pt(bpy)Cl_2$, $Pt(bpy)_2^{2+}$, and $Pt(phen)_2^{2+}$, and report here the results of our study of their electronic spectra and photophysics in solution, glass, and crystalline solid state.

Experimental Section

Preparation of Compounds. $[Pt(bpy)(en)](ClO_4)_2$, $Pt(bpy)Cl_2$, and $[Pt(bpy)_2](ClO_4)_2$ were prepared by following the method of Morgan and Burstall[1] as modified by Bielli et al.[3] The latter compound was washed several times with toluene to insure removal of unreacted ligand. All three compounds were nicely microcrystalline in appearance and gave elemental analyses in excellent agreement with their formulation as anhydrates. *Warning*! Anhydrous perchlorate salts are often shock detonators and pose a serious explosion hazard. Although we found that our preparations of these particular salts were stable toward mild shock, we suspect that polymorphism can occur in these materials, and other forms may well have dangerous properties. Use extreme care in the preparation and handling of these and other perchlorate salts! $[Pt(phen)_2]Cl_2$ was prepared in an analogous way by treating the isolated intermediate $Pt(phen)Cl_2$ with excess phenanthroline in aqueous solution. The product was isolated as a lemon yellow microcrystalline precipitate by the addition of acetone. When recrystallized slowly from hot water, the yellow trihydrate form was obtained as large gold yellow crystals, and its structure was confirmed by X-ray powder diffraction to be the same as that published by Hazell et al.[17]

Measurements. Electronic spectra were taken on a Cary 17 UV–visible spectrometer. Emission spectra were taken on a Perkin-Elmer MPF66 fluorescence spectrometer, in a right angle (solution, glass) or front surface (microcrystalline powder) configuration. Low-temperature spectra were obtained by placing the sample in a CTI closed-cycle He refrigerator. Emission spectra were corrected by the method of Parker and Rees.[18] Powder emission quantum yields were obtained by the method of Wrighton et al. and were checked against the standard emission quantum yield of $Ru(bpy)_3Cl_2$.[19] Emission lifetimes were obtained from powder samples at room temperature with a Quanta-ray DCR3 Nd:YAG frequency-tripled laser light source. The beam was severely attenuated to avoid sample heating and other effects that produce nonexponential decay, and care was taken to insure that emission intensity was linear with incident intensity. The emission was detected through Schott KV nonfluorescing cutoff filters by a Hamamatsu R928 photomultiplier tube and Tektronix 2430 digitizing oscilloscope.

Results and Discussion

Preliminary Considerations. Three types of electronic excited states must be considered as candidates for the emissive excited state of platinum(II) α-diimine complexes; they are ligand field

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(d–d), diimine (π–π^*), and metal-to-ligand charge transfer (MLCT). The possibility of a Pt (d–p) state being lowest energy in monomeric complexes may be discounted, as the $^1(d_{z^2} \rightarrow p_z)$ transition is found at quite high energies in monomeric Pt(II) complexes, e.g., 46 300 cm^{-1} (216 nm) in $PtCl_4^{2-}$[20] and 51 200 cm^{-1} (195 nm) in $Pt(NH_3)_4^{2+}$.[21]

The lowest ligand field singlet–triplet absorption in Pt(II) tetraamine complexes is found at ~35 000 cm^{-1} (285 nm).[22,23] In the corresponding *cis*-dichloroplatinum(II) diamine complexes, it is red-shifted to ~23 000 cm^{-1} (435 nm) as a consequence of the weaker ligand field.[22,23] Replacement of amine by pyridine does not affect the positions of the lowest ligand field transitions significantly; in $Pt(py)_2Cl_2$, both the lowest spin-forbidden[24a] and spin-allowed[24b] bands are at energies similar to those of the analogous complex $Pt(en)Cl_2$.[22] Therefore, we would also expect to find ligand field transitions at these energies for bis(α-diimine) and dichloro diimine complexes unless they are obscured by intense symmetry-allowed absorption features.

Emission from the lowest triplet ligand field state of *cis*-$Pt(NH_3)_2Cl_2$[25] has a maximum near 17 000 cm^{-1} (590 nm) in glassy solution at 77 K. The large Stokes shift of ~6800 cm^{-1} and full width at half-maximum (FWHM) of ~3300 cm^{-1} at this temperature are characteristic of a ligand field transition in which the excited-state geometry is very different from that of the ground state due to the antibonding nature of the LUMO. In the corresponding *cis*-$Pt(py)_2Cl_2$ complex, triplet MLCT excited states have been suggested[26] to lie at nearly the same energy as the lowest ligand field excited states, giving rise to apparent multiple-state emissions.

Intraligand $\pi \rightarrow \pi^*$ transitions can be identified by analogy to the absorption and emission spectra of the free ligand and its protonated form[27] and also by comparison with the spectra of other diimine complexes.[27-29] Zinc(II) diimine complexes[27,28a] make a particularly good choice for comparison since their spectra are free of the complications of ligand field and charge-transfer transitions. $Ir(bpy)_3^{3+}$ and $Rh(phen)_3^{3+}$ are also useful models for comparison since the lowest excited states are unambiguously ligand $\pi \rightarrow \pi^*$.[28] The identification of diimine $\pi \rightarrow \pi^*$ transitions is facilitated by the fact that they usually show pronounced vibronic structure even in fluid solution, with emission having an approximate mirror-image relationship to absorption.

The assignment of MLCT transitions is not as straightforward as the other two types of transitions. In the past, MLCT assignments have been given to absorption[16,24b,26,30] and emission[8,14,15,26] bands in the near-UV and visible spectra of several platinum(II) imine and diimine complexes, the argument being that the π-acceptor ligand(s) should have low-lying π^* orbitals. Unlike ligand-centered $\pi \rightarrow \pi^*$ and metal-centered ligand field transitions, MLCT transition energies are expected to be sensitive to solvent, and spin-allowed MLCT absorption bands have been identified in Pt(II) complexes by the solvent dependence of their absorption maxima.[16,30] Spin-forbidden MLCT transitions are more difficult to locate by this method; they are quite weak in intensity and may be located in the same energy range as other spin-forbidden ligand field and intraligand absorption bands.[26] If the lowest excited state of a complex in question is a triplet MLCT state, its emission is expected to be symmetry-allowed.[26] Thus, it can be distinguished from ligand field emission by the magnitude of its radiative rate constant. And unlike that for either ligand field or intraligand emission, the emission maximum should be solvent sensitive.

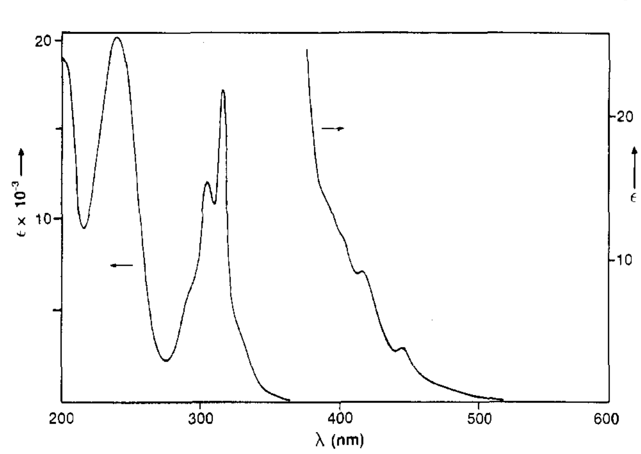

Figure 1. Absorption spectrum of $Pt(bpy)(en)^{2+}$ in aqueous solution at room temperature.

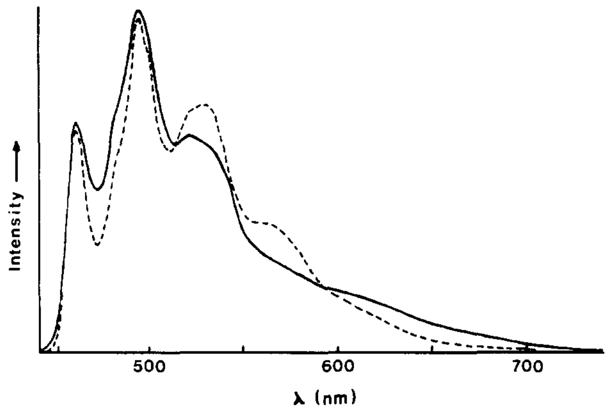

Figure 2. Emission spectra of $Pt(bpy)(en)^{2+}$ in dilute (3:1 methanol/ethanol) glassy solution at 77 K (---) and microcrystalline $[Pt(bpy)(en)](ClO_4)_2$ at room temperature (—). λ_{ex} = 360 nm.

$[Pt(bpy)(en)](ClO_4)_2$. The electronic absorption spectrum of $[Pt(bpy)(en)]^{2+}$ in aqueous solution at room temperature is shown in Figure 1. The vibronically structured feature maximizing at 316 nm is clearly the lowest energy singlet–singlet $\pi \rightarrow \pi^*$ transition of bipyridine, nearly identical with that exhibited by the complex $Zn(bpy)_3^{2+}$.[27] A second, much weaker, structured absorption has its origin at 447 nm. We assign this transition to the corresponding singlet–triplet $\pi \rightarrow \pi^*$ transition, enhanced relative to $Zn(bpy)_3^{2+}$ by platinum spin–orbit coupling ("heavy-atom" effect); $Ir(bpy)_3^{3+}$ shows a similarly enhanced singlet–triplet transition.[28]

This assignment is confirmed by a long-lived electronic emission (Figure 2), whose electronic origin at 458 nm overlaps well with the absorption origin and whose vibronic pattern, showing overlapping progressions in ~1400- and ~1000-cm^{-1} bipyridine modes, is in excellent agreement with the phosphorescence spectrum of $Zn(bpy)_3^{2+}$.[27] At room temperature, the radiative rate constant of the microcrystalline powder, calculated from a

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(29) The latter type of spectral comparison has two main advantages. First, in the case of bipyridine complexes, the diimine ligand has the nearly coplanar geometry expected in platinum(II) diimine complexes rather than the significantly noncoplanar geometry of the free ligand. Second, the electronic influence of the nitrogen lone-pair electrons is more nearly analogous if the diimine is complexed than if it is free.

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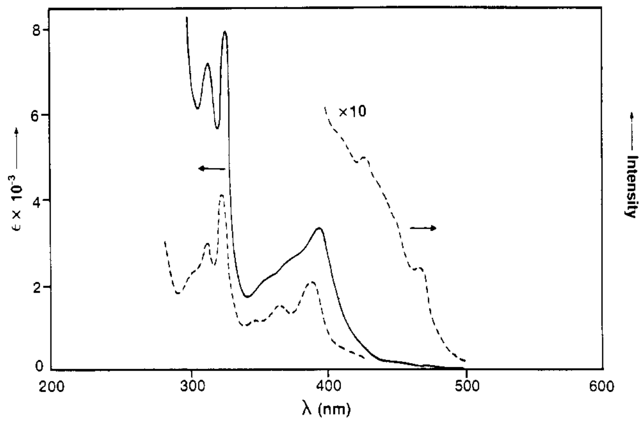

Figure 3. Absorption spectrum of Pt(bpy)Cl$_2$ in butyronitrile solution at room temperature (—) and excitation spectrum of a dilute butyronitrile glass at 77 K (---). λ_{em} = 625 nm.

measured emission lifetime of 1.4 ± 0.2 μs and quantum yield of 0.074 ± 0.003, is 5.8 × 10^4 s^{-1}, a value entirely consistent with dipole-allowed but spin-forbidden emission. The only significant difference between the emission of Pt(bpy)(en)$^{2+}$ and that of Zn(bpy)$_3$$^{2+}$ is that the former is red-shifted by ~1200 cm^{-1}, presumably due to perturbation of the bipyridine π* orbital by Pt(II) d and p$_z$ orbitals. The fact that Pt(bpy)(en)$^{2+}$ emission from the solid perchlorate salt is essentially the same as that in low-temperature glassy solution (Figure 2) indicates that there is minimal perturbation of the monomer electronic structure by crystalline packing, a situation that is atypical of platinum(II) α-diimine salts in general (vide infra).

Figure 1 also shows an intense absorption at 243 nm and a weak shoulder at ~330 nm that have no clear analogues in the absorption spectrum of Zn(bpy)$_3$$^{2+}$. Other platinum(II) bipyridine complexes also have these bands, and Gidney et al.[16] have assigned them as MLCT in the spectrum of Pt(bpy)Cl$_2$ on the basis of solvent sensitivity. Komada et al.[28c] have assigned a similar transition at ~350 nm in the absorption spectra of Ir(bpy)$_3$$^{3+}$ as MLCT.

With these assignments, we can anticipate that $^3(\pi\text{–}\pi^*)$ will also be the emissive states in platinum(II) bis(α-diimine) complexes. In complexes with a weaker ligand field, however, it is possible that the lowest energy ligand field excited state can lie below the $^3(\pi\text{–}\pi^*)$ state, as the following complex demonstrates.

Pt(bpy)Cl$_2$. This complex is well-known for its red/yellow dimorphism[1-3] in which the solid-state form has a pronounced effect on the color of the material. In solution, Pt(bpy)Cl$_2$ is yellow. The reported absorption spectrum[8,14,16] is strongly perturbed from that of Pt(bpy)(en)$^{2+}$, most likely as a consequence of the electron-donating effect of Cl$^-$ and the probable presence of Cl → Pt LMCT states[22] in the ultraviolet region of the spectrum. The most unusual feature of the absorption spectrum is an intense, very solvent-sensitive band found in the range from 345 (water) to 415 nm (chlorobenzene) and assigned by Gidney et al.[16] as a spin-allowed MLCT transition. In butyronitrile solution (Figure 3), this band is found at 394 nm (ε = 3290). Nevertheless, the lowest energy absorption feature in the absorption spectrum of Pt(bpy)Cl$_2$ is completely *insensitive* to solvent; it appears at ~475 nm (ε = 50) in both the red and yellow dimorphs of the solid,[3] in dichloromethane solution,[14] and in butyronitrile solution (ε = 60). Therefore, we can rule out the possibility that this absorption feature is the spin-forbidden component of the MLCT transition discussed above. It is less easy to distinguish between the possible assignments of this band as ligand field or $^3(\pi\text{–}\pi^*)$ based on the absorption spectrum alone. By analogy to Pt(en)Cl$_2$[21,22] and *cis*-Pt(py)$_2$Cl$_2$,[26] this complex is expected to have a lowest singlet–triplet ligand field transition near 23 000 cm^{-1}, very close in energy to the lowest singlet–triplet π → π* transition found in Pt(bpy)(en)$^{2+}$ above.

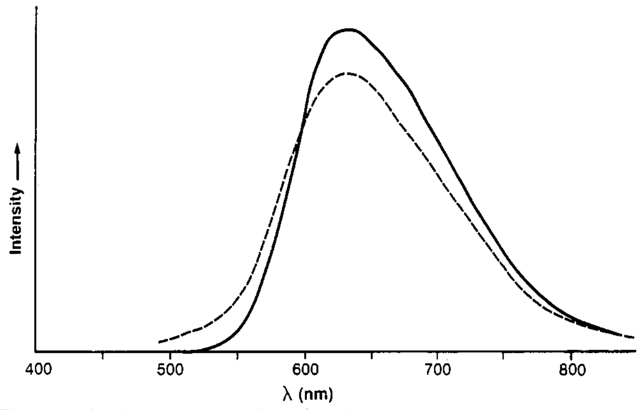

Figure 4. Emission spectra of Pt(bpy)Cl$_2$ in dilute glassy butyronitrile solution at 77 K (—) and in the yellow microcrystalline solid state at 77 K (---). λ_{ex} = 360 nm.

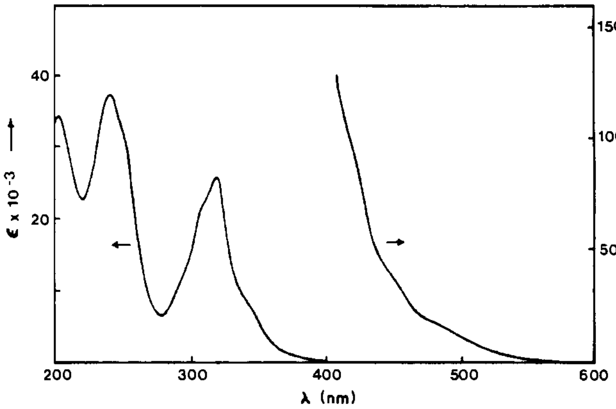

Figure 5. Absorption spectrum of Pt(bpy)$_2$$^{2+}$ in aqueous solution at room temperature.

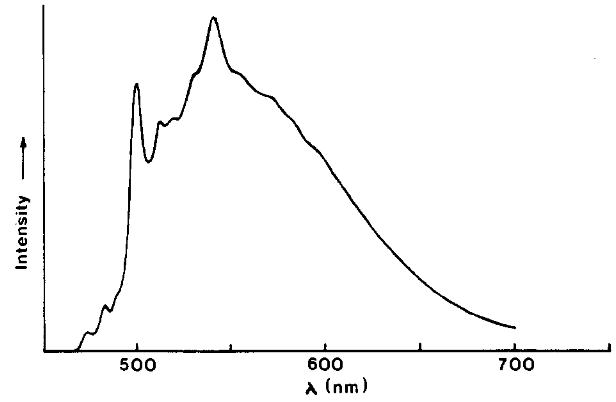

Figure 6. Emission spectrum of microcrystalline [Pt(bpy)$_2$](ClO$_4$)$_2$ at 30 K. λ_{ex} = 314 nm.

The emission from this complex is vanishingly weak at room temperature. However, at 77 K, a broad unstructured emission (Figure 4) is observed from dilute glassy solutions and from both the red and yellow microcrystalline forms.[8,31] The complete lack of solvent sensitivity of this emission shows that it does not originate from a MLCT excited state. The large Stokes shift and lack of

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(31) In ref 8, the authors report an anomalous emission spectrum for Pt(bpy)Cl$_2$ in frozen methanol at 77 K. We were unable to reproduce this result. In methanol glass at 77 K, we find a weak, structureless emission with a maximum at 610 nm and a corrected fwhm of ~3600 cm^{-1}. No emission is detectable below 500 nm. This is in keeping with our emission results from ethanol–methanol glass (emission maximum 615 nm), butyronitrile glass (625 nm, Figure 4), yellow solid (624 nm) and red solid (613 nm). In the case of the solid forms, our findings are in agreement with ref 8. The possibility that the glassy solution emission is really coming from a microcrystalline precipitate is discounted by our results in butyronitrile. Unlike the alcoholic glasses, Pt(bpy)Cl$_2$ is quite soluble in this glass, and the emission is considerably more intense than in alcoholic glasses at comparable dilution. At high dilution, we obtained the absorption, emission, and excitation spectra shown in Figures 3 and 4. The particularly good match between the solution absorption and glass excitation spectrum is strong evidence that the low-temperature glass is a true solution.

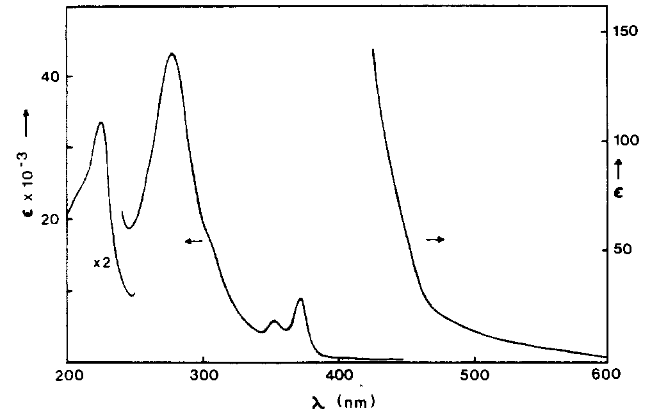

Figure 7. Absorption spectrum of $Pt(phen)_2^{2+}$ in aqueous solution at room temperature.

vibronic structure of the emission clearly mark it as a ligand field emission, and it has a energy and bandwidth similar to those of the ligand field emission observed from *cis*-$Pt(NH_3)_2Cl_2$.[25]

$[Pt(bpy)_2](ClO_4)_2$. The absorption spectrum of this complex in acetonitrile at room temperature (Figure 5) is very similar to that of $Pt(bpy)(en)^{2+}$, molar extinction coefficients simply being higher, and the same electronic assignments are suggested. Evidently, interaction between the two slightly noncoplanar[32] ligands is minimal. The emission of $[Pt(bpy)_2](ClO_4)_2$ is undetectably weak at room temperature in either the solid state or in solution. Moreover, we were unable to make a true low-temperature glassy solution of the complex due to the tendency of this sparingly soluble salt to crystallize out of solution as the temperature was lowered. The emission spectrum of the microcrystalline powder at 30 K is shown in Figure 6. A complicated pattern of vibronic structure is seen on the high-energy side of the band, the frequencies of ~1450, ~700, and ~400 cm^{-1} being consistent with bipyridine vibrational modes. There appear to be two emission origins, at 472 and 498 nm, the former agreeing with the excitation spectrum origin. The multiple origins could be due to spin–orbit splitting of the emissive state (as has been noted for $Ru(bpy)_3^{2+}$ [33]), or it could indicate multiple emission sites and possible crystal polymorphism.

The low-energy side of the emission band is asymmetric and appears to conceal a broad structureless emission. This structureless feature could indicate multiple-state emission from this complex, as is seen in platinum(II) pyridyl complexes.[26] However, we have seen this type of feature in the solid-state spectra of other platinum(II) α-diimine spectra where it is absent in the solution emission spectrum and suspect that it is an excimer-like emission from neighboring complexes that are brought into electronic contact by the crystal packing. This assignment will be discussed in greater detail for the case of $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ in the folllowing section. Whether it is a feature of one particular crystalline polymorph or whether it is present in the spectra of all crystalline forms is not known at this point. Our lack of knowledge of the crystal structure of $[Pt(bpy)_2](ClO_4)_2$, together with the lack of solution emission data, restricts our assignment to conjecture.

$[Pt(phen)_2]Cl_2$. The absorption spectrum of $Pt(phen)_2^{2+}$ in aqueous solution at room temperature is shown in Figure 7. The $\pi \rightarrow \pi^*$ spectrum of phenanthroline is more complicated than that of bipyridine[27] which makes interpretation more difficult. The overall absorption spectrum of $Pt(phen)_2^{2+}$ is closely analogous to that of $Rh(phen)_3^{3+}$;[28b] the intense band at 267 nm has a counterpart at ~275 nm in the Rh(III) complex, and several weaker spin-allowed transitions are seen at lower energy in both spectra. Since there is no band in the spectrum of $Pt(phen)_2^{2+}$

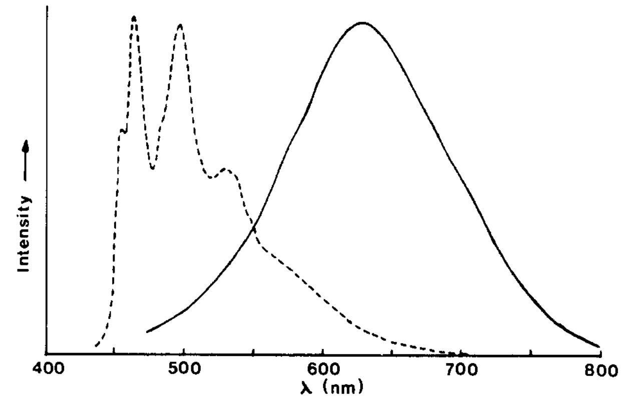

Figure 8. Emission spectra of $Pt(phen)_2^{2+}$ in dilute glassy (3:1 methanol/ethanol) solution at 77 K (---) and microcrystalline $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ (—) at 77 K. λ_{ex} = 360 nm.

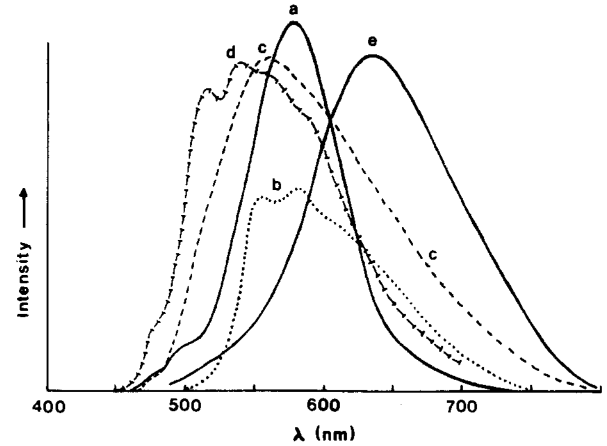

Figure 9. Emission spectra of different microcrystalline samples of $[Pt(phen)_2]Cl_2$ prepared and stored under various conditions, showing the sensitivity of spectrum to preparation and storage history (see text). The intensity was arbitrarily normalized; actual intensities may vary by several orders of magnitude from sample to sample. λ_{ex} = 360 nm.

that is clearly *absent* in the spectrum of $Rh(phen)_3^{3+}$, the location of MLCT transitions cannot be positively identified. Most likely, they are obscured by the more intense intraligand transitions. As far as the lowest excited state is concerned, the energies of the lowest $\pi\pi^*$ excited state of bipyridine and phenanthroline are nearly equal,[27,28] and so the lowest $^3(\pi-\pi^*)$ states of $Pt(phen)_2^{2+}$ and $Pt(bpy)_2^{2+}$ are expected to occur at comparable energies. In accord with this, we see an ill-resolved weak absorption shoulder at ~450 nm that is presumably the singlet–triplet $\pi \rightarrow \pi^*$ transition. The assignment of the lowest excited state as $^3(\pi-\pi^*)$ is borne out by the emission spectrum of $Pt(phen)_2^{2+}$ in glassy solution at 77 K (Figure 8a), which is completely analogous to that of $Pt(bpy)(en)^{2+}$ under the same conditions.

The emission spectrum of solid $[Pt(phen)_2]Cl_2$ is very sensitive to sample preparation and history, as can be seen in Figure 9. The trihydrate, obtained by slow recrystallization from water and verified by X-ray powder diffraction to have the structure published by Hazell et al.,[17] gives the broad (fwhm = 4200 cm^{-1}), featureless emission spectrum at 77 K shown in Figure 8b. As with $[Pt(bpy)_2](ClO_4)_2$, its emission is virtually undetectable at room temperature but is easily seen at low temperature. In contrast to the trihydrate, the anhydrate obtained by fast precipitation of $[Pt(phen)_2]Cl_2$ from water by acetone has an intense emission at room temperature (quantum yield > 0.01) that has a nonexponential decay with lifetime(s) on the order of 1–2 μs. The emission spectrum is a single peak with a maximum at 578 nm and a half-width of 2400 cm^{-1} (Figure 9a). To further complicate the picture, the spectrum of an anhydrate sample that is several weeks old has the 578-nm maximum but shows an additional peak at 555 nm and a shoulder at ~620 nm (Figure 9b). We interpret these results as evidence of polymorphism in $[Pt(phen)_2]Cl_2$, most likely dependent upon the number of waters

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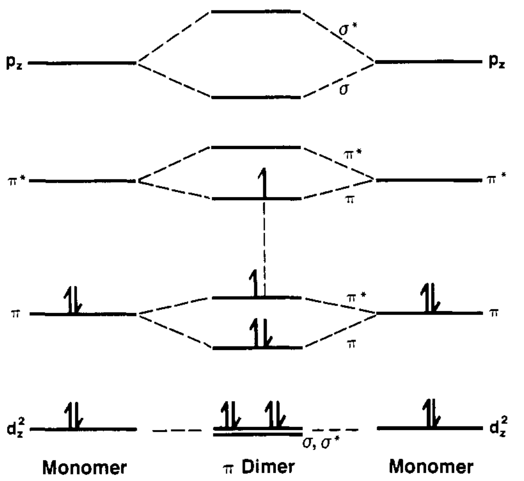

Figure 10. Schematic interaction of orbitals in Pt-ligand π dimers.

of hydration, which seems to be a dynamic variable in the solid state.

The emissions of all microcrystalline forms of $[Pt(phen)_2]Cl_2$ are significantly red-shifted from those seen in glassy solution; moreover, the solid-state emission profiles are much broader and are unstructured. These observations are reminiscent of excimer emission from planar aromatic molecules and indicate a marked effect of the crystal structure upon the electronic structure of the monomeric complex. In the case of $[Pt(phen)_2]Cl_2 \cdot 3H_2O$, the cations are known to crystallize in discrete, weakly interacting face-to-face dimers similar to those of *cis*-bis(2-phenylpyridine)platinum(II) mentioned in the introduction,[9] with a Pt-Pt distance of 3.710 Å.[17] This distance is too long to support significant metal-metal interaction, but is close enough to allow overlap of phenanthroline π^* orbitals. Thus, we suggest that the solid-state emission of this form is due to a classical excimeric interaction of the phenanthroline ligands in the two monomers. This situation is diagramed in Figure 10. Here, metal-metal interaction is negligible and the ground-state interaction between the phenanthrolines is very weak. However, the lowest energy $\pi \rightarrow \pi^*$ excitation results in a state that has net bonding character between the phenanthrolines of the two complexes.

The excitation spectrum of $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ at 77 K is actually only very weakly perturbed from that of the room-temperature solution absorption spectrum, and similar behavior has been noted for solution aggregates of metal α-diimine complexes.[34] The lowest energy feature in the excitation spectrum is a band at 463 nm, compared to the absorption spectrum shoulder at ~450 nm. Thus, the crystal chromophore probably collapses, to the extent allowed by the lattice, to a shorter phen-phen distance in the excited state. This is typical excimer behavior.[35]

Conclusions

For dilute solution, we have observed two types of emission behavior for Pt(II) complexes containing α-diimine ligands. If the complex also has weak field ligands such as chloride, ligand field (d-d) excited states become the lowest energy excited states. If only strong field ligands are present, a diimine $^3(\pi-\pi^*)$ state becomes the lowest. In no case we have studied does an MLCT excited state lie lowest. The earliest assignments of MLCT emission from platinum α-diimine complexes[8,14,15] were based largely upon solid-state emission spectra, which we have shown to be strongly perturbed from solution spectra in two representative complexes.

In the solid state, absorption and emission spectra of Pt(II) complexes are seldom analogous to those of solutions. Direct Pt-Pt interactions can cause strong splitting of d_{z^2} orbitals,[11-13] which can strongly perturb the ligand field, (d-p), and/or MLCT excited states. What we wish to emphasize here is that there is another type of electronic interaction, namely ligand-ligand excimeric interaction, that may also strongly perturb emission spectra. Thus, the observation of solid-state effects in the emission spectra of d^8 complexes does not necessarily indicate metal-metal interaction. The distinctly different effects of strong metal-metal interaction for platinum(II) α-diimine complexes will be discussed by us in a future paper.

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Registry No. $[Pt(bpy)(en)](ClO_4)_2$, 54806-37-0; $Pt(bpy)Cl_2$, 13965-31-6; $[Pt(bpy)_2](ClO_4)_2$, 18437-39-3; $[Pt(phen)_2]Cl_2$, 59981-72-5.

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Electrochemical Assembly of Metallopolymeric Films via Reduction of Coordinated 5-Chlorophenanthroline

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Electrochemical reduction of iron, osmium, and ruthenium complexes containing the ligand 5-chlorophenanthroline leads to the controlled growth of metallopolymers as electrode coatings. The coatings are electroactive and display a reversible electrochromic effect upon metal oxidation. Auger electron spectroscopy studies show that the polymerization mechanism involves carbon-chlorine bond cleavage and the generation of exchangeable chloride ions. The proposed linkage mechanisms involve direct carbon-carbon coupling of phenanthroline ligands. The possible utility of these new polymers in redox conductivity studies and in microstructure fabrication is noted.

Introduction

Electroactive metallopolymeric films are unique materials that have generated tremendous interest in the decade or so since their initial appearance.[1] Their development, especially as electrode coatings, has been motivated both by perceived opportunities in applications chemistry (e.g., electronic devices,[2] electrochromic technology,[3] chemical analysis,[4] electrocatalysis,[5] visible-light

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