transition in $Pd(en)Cl_2$ was not observed here.

The orbitals thought to be involved in the transitions observed here have been identified in terms of their major atomic orbital components. As the discussion of the assignment of the 44.5 × 10^3 cm^{-1} band indicates, mixing between these components is anticipated. A given molecular orbital is thus expected to be more complex than is implied by, for instance, functions 1–6, as Jørgensen has illustrated in his discussion of the $L(\pi_h) \rightarrow M$ transition of $PdCl_4^{2-}$ possibly acquiring intensity through interaction of π_h and σ molecular orbitals.[21b] It is thought, however, that the assignments developed here provide basically correct insights into the nature of the transitions involved.

The in-plane spectra of $Pt(en)Cl_2$ shown in Figure 1 are both seen to rise to modest maxima in the high-energy region. These peaks are neither sufficiently pronounced nor sufficiently well characterized to be suitable for Kramers–Kronig analysis. It is likely, however, that, as was concluded in the case of K_2PtCl_4,[5] $Pt(en)Cl_2$ shows in-plane absorption in the 45 × 10^3 cm^{-1} region. Whether the weakness of this absorption reflects that one is merely observing the onset of charge-transfer absorption or that the platinum compound's charge-transfer bands tend to be less intense than those of the palladium compound is not clear at this point.

Acknowledgment. The authors wish to express their appreciation to Dr. Richard J. Majeste, who carried out the X-ray crystallographic structure verification and face identification described in the Results and Discussion. A grant of computer time from the University of New Orleans Computer Center is also gratefully acknowledged.

Registry No. $Pt(en)Cl_2$, 14096-51-6; $Pd(en)Cl_2$, 15020-99-2.

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Multistate Luminescence, Absorption, and MCD Studies of the Relative Energies of d → d, d → π^*, and n, $\pi \rightarrow \pi^*$ Transitions for the Cis and Trans Isomers of Dichlorobis(pyridine)platinum(II)

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Received January 4, 1982

Luminescence, absorption, and magnetic circular dichroism (MCD) experiments are reported for the cis and trans isomers of dichlorobis(pyridine)platinum(II). For the trans isomer, an analysis of the temperature dependence of the lifetimes and luminescence intensities indicates that emission at 605 nm is from two excited π^* states separated by 240 cm^{-1}. For the cis isomer, time-resolved spectroscopy has allowed us to observe two emission bands at 600 and 700 nm, which are assigned from their lifetimes to $\pi^* \rightarrow d$ and $d \rightarrow d$ transitions, respectively. Further, temperature dependent lifetime studies show that the 600-nm band ($\pi^* \rightarrow d$) is from two electronic states separated by 200 cm^{-1}. The absorption spectra of both isomers has been measured at room and low temperatures in solution, in glasses, and in KCl pellets. From a comparison of the pyridine and $Pt(NH_3)_2Cl_2$ absorption and MCD spectra with MO calculations, the observed absorption bands for $Pt(py)_2Cl_2$ are assigned as $d \rightarrow d$, $d \rightarrow \pi^*$, and n, $\pi \rightarrow \pi^*$ transitions. For the cis isomer the lowest unoccupied molecular orbital is shown to be a d metal orbital.

Introduction

In a series of papers[1-7] we have reported the absorption and luminescence spectra of selected platinum complexes. In particular, we have recently studied the cis and trans isomers of dichlorodiammineplatinum(II),[7] where NH_3 is a σ-bonding ligand. In this paper we discuss the cis and trans isomers for dichlorobis(pyridine)platinum(II), where pyridine is a π-donor ligand. Luminescence, absorption, and MCD experiments and MO calculations have been carried out to understand the electronic structure of $Pt(py)_2Cl_2$.

Konig and Schlafer[8] have previously studied the reflectance and solution spectra of the cis and trans isomers of $Pt(py)_2Cl_2$. The bands at 27 400 (cis) and 27 300 cm^{-1} (trans) were assigned as singlet–singlet d–d transitions while the bands at 33 560 (cis) and 34 720 cm^{-1} (trans) were assigned to charge-transfer $d \rightarrow \pi^*$ transitions. For absorptions higher than 38 460 (cis) or 37 650 cm^{-1} (trans) the assignments were to pyridine ($\pi \rightarrow \pi^*$) transitions. More recently, Textor and Ludwig[9] have studied the diffuse-reflection spectra of the cis and trans isomers and assigned the two shoulders at lower energy (23 500 and 27 400 cm^{-1} for the trans isomer and 22 000 and 28 200 cm^{-1} for the cis isomer) as two spin-forbidden ligand field transitions. In 1976 Ibusuki and Saito[10] reported Hückel MO calculations for both $Pt(py)_2Cl_2$ and $Hg(py)_2Cl_2$. It is not clear from the MO calculations whether the LUMO is a Pt d orbital or a pyridine π^* orbital. Experimental data are needed to establish the answer to this question.

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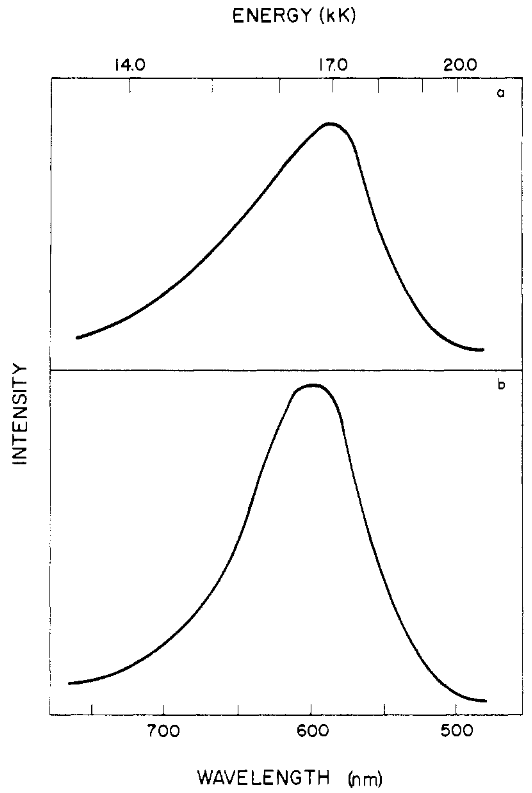

Figure 1. Luminescence spectra of the (a) cis and (b) trans isomers of dichlorobis(pyridine)platinum(II) in KBr pellets at 78 K.

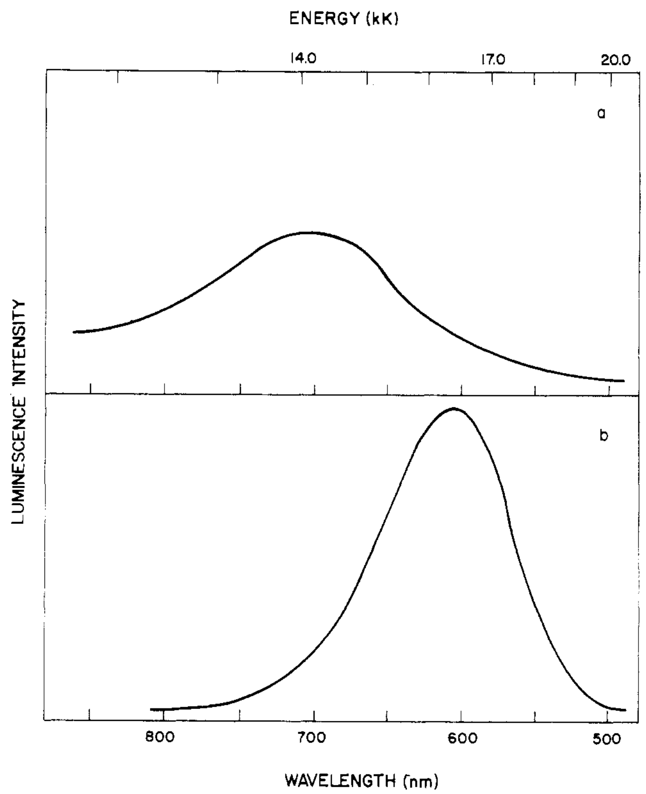

Figure 2. Time-resolved luminescence spectra of *cis*-Pt(py)$_2$Cl$_2$ at 78 K for time delays of (a) 10 μs and (b) 2 ms. A N$_2$ laser has been used for excitation of a single crystal at 337 nm. The excitation direction was perpendicular to the long axis of the crystal, and emission was observed parallel to the long crystal axis.

Experimental Methods

cis-Pt(py)$_2$Cl$_2$ was prepared by the method of Kauffman and Cowan.[11] K$_2$PtCl$_4$ was reacted with an aqueous solution of pyridine to produce *cis*-Pt(py)$_2$Cl$_2$. The *trans*-Pt(py)$_2$Cl$_2$ isomer was prepared by the method of Durig.[12] An aqueous solution of pyridine was added to an HCl solution of K$_2$PtCl$_4$ to produce Pt(py)$_4$Cl$_2$, which was treated with HCl to precipitate *trans*-Pt(py)$_2$Cl$_2$. Crystals of both isomers were grown by dissolving the isomer in DMF at about 50 °C and slowly cooling the solution to room temperature.

Absorption experiments were done with glasses of ethanol and frozen solutions of methylene chloride. Liquid nitrogen was used as the coolant. The solutions were cooled in a cell made from clear fused rectangular quartz tubing with an inside diameter of 3 by 5 mm. The cell, with a tightly fitting cork top to prevent evaporation of the solvent, was placed in the sample holder of an Air Products LT-3-110 liquid helium transfer Heli-Tran and cooled slowly without a vacuum pump until the solutions solidified; at this point the vacuum pump was turned on. Ethanol formed a clear glass when it froze, which allowed spectra to be recorded at temperatures as low as 77 K. In contrast, methylene chloride became opaque when it froze so spectra could only be recorded as low as the freezing point of methylene chloride.

For the luminescence experiments a Molectron Corp. UV 14 Series II pulsed nitrogen laser was used. The laser beam has a wavelength of 337.1 nm and a pulse width of about 10 ns. The samples were excited directly by the laser beam with the detector system perpendicular to the incident beam. The detector system consists of a McPherson Model 2051 monochromator and a PAR Model 124A lock-in amplifier and an RCA 31034 (A-20 response) photomultiplier detector. For the lifetime measurements a Model 162 PAR boxcar integrator was used with a PAR Model 164 processor module. An external homemade dual trigger was used to pretrigger the boxcar approximately 600 ns prior to triggering the N$_2$ laser. Lifetimes greater than 10 ns can be measured with this setup.

The absorption experiments were carried out on a Cary 17D spectrophotometer. Temperature-dependent absorption and luminescence experiments were made with an Air Products LT-3-110 liquid helium transfer Heli-Tran. The temperature of a sample was monitored with a thermocouple attached to a silver plate on which a sample was attached with Cryo-Con grease. MCD experiments were performed with a Cary 60 spectropolarimeter with a Cary MCD accessory and a Westinghouse 60-kG superconducting magnet.

Luminescence Studies

The uncorrected luminescence spectra of the cis and trans isomers of dichlorobis(pyridine)platinum(II) in KBr pellets at 78 K are shown in Figure 1. For the trans isomer, luminescence is first observed at 510 nm with the luminescence maximum at 605 nm. Unlike the trans isomer, *cis*-Pt(py)$_2$Cl$_2$ has an asymmetric luminescence band. For the cis isomer the luminescence maximum is observed at 590 nm with the luminescence first appearing at 510 nm.

With use of time-resolved spectroscopy the luminescence spectra can be studied as a function of time. When the luminescence spectra are recorded at different time delays, the luminescence is resolved into more than one component. The positions of the luminescence maxima of these components may then be determined.

Time-resolved spectroscopy has been successfully used to resolve the asymmetric luminescence band of *cis*-Pt(py)$_2$Cl$_2$. In Figure 2 are shown the luminescence spectra at time delays of 10 μs and 2 ms. At a time delay of 2 ms there is a component with a luminescence maximum at 605 nm, and for a time delay of 10 μs there is a component with a luminescence maximum at 700 nm. The 605-nm component, which appears at the longer time delay, is about twice as intense as the 700-nm component with the shorter time delay. Lifetimes were also measured for the two time-resolved components at 78 K. At this temperature the 605-nm component has a lifetime of 390 μs while the 700-nm component has a much shorter lifetime of about 20 μs.

The luminescence spectra for both the cis and the trans isomers of Pt(py)$_2$Cl$_2$ were recorded as a function of temperature. The relative intensity of the luminescence vs. tem-

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[11] G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 7, 241 (1963).

[12] J. R. Durig, B. R. Mitchell, D. W. Sink, J. N. Willis, Jr., and A. S. Wilson, *Spectrochim. Acta, Part A*, 23A, 1121 (1967).

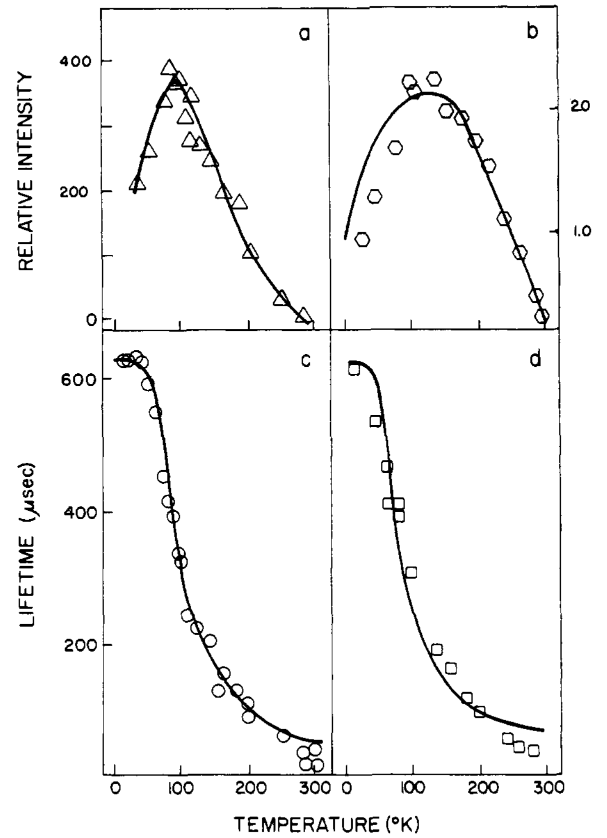

Figure 3. Variation of luminescence intensity and lifetime vs. temperature for (a and c) the trans isomer and (b and d) the cis isomer. Here the sample (single crystal or KBr pellet) is excited with an N_2 laser at 337 nm. For (c) and (d) the solid curve is a fit of eq 2 to the experimental data.

perature for the trans and cis isomers is shown in Figure 3a,b. For both isomers there is an initial increase in the intensity as the sample is cooled. A maximum is reached at 80 K for the trans isomer and at 120 K for the cis isomer. As the temperature is lowered to 5 K, there is a decrease in the intensity. Also, in parts c and d of Figure 3 are plotted lifetime vs. temperature data for the trans and cis isomers, respectively.

The temperature dependence of the luminescence intensity and lifetime data was analyzed as follows.[7] Luminescence is assumed to be from the superposition of emissions from low-lying excited electronic states. Depopulation of these low-lying states can be expressed as

$$\frac{-\mathrm{d}N}{\mathrm{d}t} = \sum_{i=1}^{p} K_i n_i \qquad (1)$$

N is the total population of the excited electronic states at time t, n_i is the population of the ith state, p is the no. of excited states, and K_i is the total rate constant for depopulation of the ith level to the ground state. Both temperature-dependent and temperature-independent rate constant models were considered. The model for both isomers that gave the best fit of the experimental lifetime data is a model in which emission is assumed to occur from two excited electronic states separated by an energy ΔE with rate constants independent of temperature. In this case, the expression for the lifetime vs. temperature is

$$\tau(T) = \frac{1 + e^{-E/kT}}{K_1 + K_2 e^{-\Delta E/kT}} \qquad (2)$$

Values for K_1, K_2, and ΔE were obtained by fitting the experimental τ vs. T data to eq 2 with use of the Simplex method.[13] For the trans isomer, $K_1 = 0.0016$ μs^{-1}, $K_2 = 0.056$ μs^{-1}, and $\Delta E = 236$ cm^{-1}; also, for the 600-nm peak of the cis isomer, $K_1 = 0.0016$ μs^{-1}, $K_2 = 0.049$ μs^{-1}, and $\Delta E = 205$ cm^{-1}.

Comparison of the 600-nm lifetime results for the trans isomers of $Pt(NH_3)_2Cl_2$ and $Pt(py)_2Cl_2$ indicates significant differences in the number of emitting states, their relative energies, and rate constants. We have previously shown that emission at 600 nm for the trans amine isomer occurs from three emitting d states with relative energies of 0, 157, and 337 cm^{-1} and K_i values of 0.057, 0.50, and 1.30 μs^{-1}, respectively. For the amine case the lowest energy crystal field transition, $d_{xy} \rightarrow d_{x^2-y^2}$, gives rise to a $^3B_{1g}$ term with D_{2h} symmetry, which in the presence of metal spin–orbit interaction will result in $(B_{1g}) \times (B_{1g},B_{2g},B_{3g}) = A_g + B_{2g} + B_{3g}$ states. The B_{2g}, B_{3g} states can undergo a transition to the A_{1g} ground state by an electric dipole mechanism with coexcitation of B_{1u} and B_{2u} vibrations while the $A_{1g} \rightarrow A_{1g}$ transition can occur with coexcitation of B_{1u}, B_{2u}, and B_{3u} vibrations. With a vibronic transition, the A_g and B_{3g} electronic states can mix with the B_{2u} state at 50 000 cm^{-1} ($\epsilon = 6500$ cm^{-1} M^{-1}) while the B_{2g} state can mix with the B_{3u} state at 45 500 cm^{-1} ($\epsilon = 2700$ cm^{-1} M^{-1}); thus, it is reasonable that the A_g and B_{3g} emitting states have a different K_i value than the B_{2g} state.

Let us now determine how a d → π^*(py) transition can be responsible for the 600-nm emission of trans-$Pt(py)_2Cl_2$. The lowest unoccupied π^* MO for pyridine belongs to b_2 symmetry in the C_{2v} point group, and when two such MO's are combined for the trans isomer with the D_{2h} point group, the result is b_{1g} and b_{3u} symmetry states. A transition from the highest filled b_{1g} (xy) molecular orbital to the b_{3u} π^* MO gives rise to a $^3B_{2u}$ electronic state, which, after spin and orbital components are coupled, yields A_{1u}, B_{1u}, B_{3u} resulting states. Since the electric dipole moment operator transforms as (B_{1u}, B_{2u}, B_{3u}) irreducible representations, the $A_{1g} \rightarrow A_{1u}$ transition is forbidden by an ED mechanism but the $A_{1g} \rightarrow B_{1u}$, B_{3u} transitions are allowed. From our experimental data for the pyridine ligand (trans isomer) we conclude that the A_{1u} spin–orbit state is lowest in energy with the B_{1u}, B_{3u} states at higher energy. Similar results are obtained for the 600-nm emission of the cis $Pt(py)_2Cl_2$ isomer. We conclude that the splitting between the B_{2u} and B_{3u} states must be large enough so that the higher energy state is not thermally populated at 300 K or, alternatively, the K_i values for the B_{2u} and B_{3u} states are equal.

We have attempted to analyze the luminescence intensity data vs. temperature for the radiative rate constants as in the amine case.[7] However, unlike for the cis ammine, we were unable to obtain a calculated fit of the experimental data with either a two- or a three-state model. These results suggest that as the temperature changes the relative amount of emission due to d → d vs. π^* → d changes. Further, it is significant to point out that when the wavelength of excitation is changed from $\lambda = 337$ nm to UV Xe light excitation, the intensity data vs. temperature changes with now less change of intensity with changing temperature. This indicates the decay pathways are a function of excitation energy. Finally, when the excitation wavelength is 337 nm but the sample is changed from a single crystal to a KBr pellet with the appropriate isomer, the measured lifetimes vs. temperature do not vary; here, the molecular environment is less important than the excitation energy. The intermolecular environment change is unimportant because the lattice vibrational modes (≤ 100 cm^{-1}) are not important for the radiative lifetime values.

MCD and Absorption Studies

MCD Studies. In Figure 4 we show the absorption and MCD spectra for the cis and trans isomers of dichlorobis-

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(13) S. L. S. Jacoby, J. S. Kowalik, and J. T. Pizzo, "Iterative Methods for Nonlinear Optimization Problems", Prentice-Hall, Englewood Cliffs, NJ, 1972, pp 79–83.

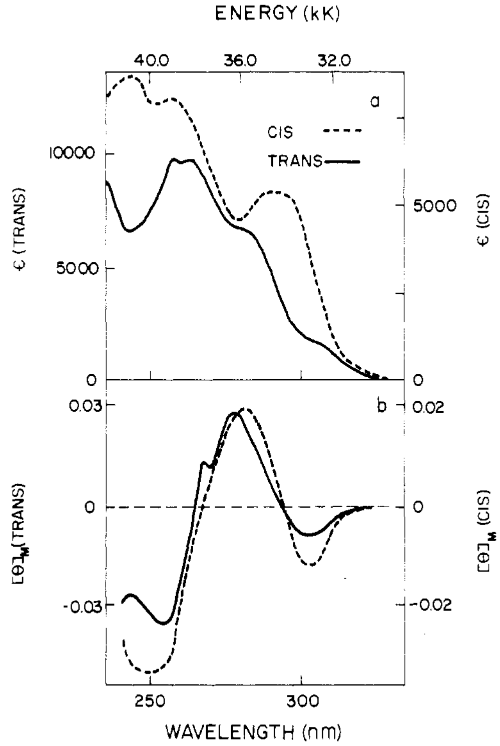

Figure 4. Room-temperature (a) absorption and (b) MCD spectra for the cis and trans isomers of dichlorobis(pyridine)platinum(II) in a methylene chloride solvent. The units of $[\Theta]_M$ are cm^2 mol^{-1} G^{-1}.

(pyridine)platinum(II) in methylene chloride solvent at room temperature. Due to the low C_{2v} symmetry for the cis isomer and D_{2h} symmetry for the trans isomer, there are no degenerate ground or excited electronic states. Thus, only MCD *B* parameters will be observed. Recent MCD spectral results[14] for just pyridine in a room-temperature *n*-heptane solution shows a negative *B* term at 34 800 cm^{-1} and a positive term at 40 000 cm^{-1}. The 34 800-cm^{-1} band was assigned to the $^1B_1$ n → π* transition while the 40 000-cm^{-1} band was assigned to the lowest energy $^1B_2$ π → π* transition. In contrast, for the $Pt(py)_2Cl_2$ isomers, Figure 4 shows a negative *B* term for both isomers at 35 300 cm^{-1}, along with a positive *B* term, which appears near 40 000 cm^{-1} in these complexes. Thus, because of the same *B* signs and energies for the two bands in both pyridine and the $Pt(py)_2Cl_2$ isomers, we assign these two bands in the isomers as n → π* and π → π* transitions, respectively.

Absorption Results. In Figure 5 absorption spectra are shown for *trans*-$Pt(py)_2Cl_2$ in (a) ethanol at 78 K and (b) a KCl pellet at 5 K; also, absorption spectra are shown for *cis*-$Pt(py)_2Cl_2$ in (c) methylene chloride at 169 K and (d) a KCl pellet at 5 K. In Figure 6 we show the absorption and derivative spectra for the trans isomer in methylene chloride in a 10-cm cell at about 27 500 cm^{-1}, where a weak transition was observed.

Molecular Orbital Calculations. Previously, iterated extended Hückel molecular orbital calculations have been carried out by Ibusuki and Saito[10] for planar *trans*-$Pt(py)_2Cl_2$ but not for the cis isomer. The difficulty with these calculations is twofold. First, we expect that in solution the trans isomer is not planar because the crystal structure of the trans complex is known to have the pyridine rings 56.2° out of the molecular plane and give rise to D_2 symmetry. Secondly, extended Hückel results for pyridine predicts the N lone-pair orbital to be the HOMO followed by a σ(C–H) orbital. The two π type orbitals are below these. In contrast, photoelectron (PES) results for pyridine indicate an ordering where the π(a$_2$) orbital and the N lone pair are the highest occupied molecular orbitals and appear nearly degenerate. These are followed in decreasing energy by another π(b$_1$) orbital and a σ orbital (b$_2$) involving carbon and hydrogen bonding.

Table I. Extended Hückel Parameters Used in This Paper

orbital	H_{ii}, eV	exponent	orbital	H_{ii}, eV	exponent
Pt[a] 6s	−9.80	2.60	N 2s	−27.50	1.875
Pt 6p	−5.35	2.45	N 2p	−14.49	1.65
Pt 5d	−10.61	3.15	C 2s	−21.43	1.55
Cl 3s	−25.23	2.183	C 2p	−11.42	1.325
Cl 3p	−13.24	1.733	H 1s	−13.6	1.200

[a] Reference 13.

Molecular orbital calculations using the experimental ground-state structures of C_2 (cis isomer) and D_2 (trans isomer) for dichlorobis(pyridine)platinum were carried out with use of the charge-iterated extended Hückel method. Slater type orbital exponents and valence state ionization potentials employed in this calculation are listed in Table I for Pt, Cl, N, C, and H.

These calculations were done to provide a comparison with Ibusuki and Saito's results. It is important to point out that the MO calculations have not been used to assign transitions for pyridine because of the reported difficulties of treating pyridine by an extended Hückel model.[15] However, the MO calculations have been used to give the correct ordering and energy separations for the d orbitals because of our previous results for $Pt(NH_3)_2Cl_2$.[7]

Figure 7 shows the calculated MO diagrams for both isomers. In both cis and trans isomers, the d orbital that is directed toward the ligand is highest in energy and hence unoccupied in the d^8 system. With the axis system as shown in Figure 7, we see this is the $d_{x^2-y^2}$ orbital in the trans isomer and the d_{xy} orbital in the cis isomer.

The unoccupied MOs are predicted from the MO calculations to have the π* pyridine orbital lowest in energy, followed by the $d_{x^2-y^2}$ (trans) and d_{xy} (cis) orbitals. Still higher in energy are another set of unoccupied π* orbitals for both the trans and cis isomers.

Analysis of Absorption Spectra. For both the cis and the trans isomers of dichlorobis(pyridine)platinum(II) three types of electronic transitions can occur in the vis–UV spectrum: (1) transitions within states centered on the pyridine molecule, (2) transitions from the filled d states to the pyridine π* states, and (3) transitions between the filled d states and the empty d or p states. The first type of transition has already been considered in the MCD discussion.

Next, we will assign the platinum to pyridine d → π* transitions. The MO results in Figure 7 indicate that the relative d-level spacing for *cis*- and *trans*-$Pt(py)_2Cl_2$ is the same as for the appropriate isomers of $Pt(NH_3)_2Cl_2$. Since the NH_3 and pyridine ligands are of about equal strength in the spectrochemical series, this result is reasonable. It is known for pyridine[14] that the LUMO π* is separated from the next higher energy π* state by 10 000 cm^{-1}.

In Table II are given the low-energy symmetry-allowed d → π* transitions. These results have been derived by use of C_{2v} and D_{2h} character tables. The observed absorption maxima with $\epsilon > 1000$ cm^{-1} M^{-1} in the spectra of *cis*- and *trans*-Pt(py)$_2$Cl$_2$ which have not been assigned to n, π → π* pyridine transitions must be assigned as d → π* rather than d → d transitions because of the small ε values for d–d transitions for $Pt(NH_3)_2Cl_2$.[7] For the *trans*-$Pt(py)_2Cl_2$ isomer in ethanol at 78 K two strong transitions are found at 32 300 and 37 600

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(14) A Kaito, M. Hatano, and A. Tajiri, *J. Am. Chem. Soc.*, **99**, 5241 (1977).

(15) W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *Chem. Phys.* **10**, 345 (1975).

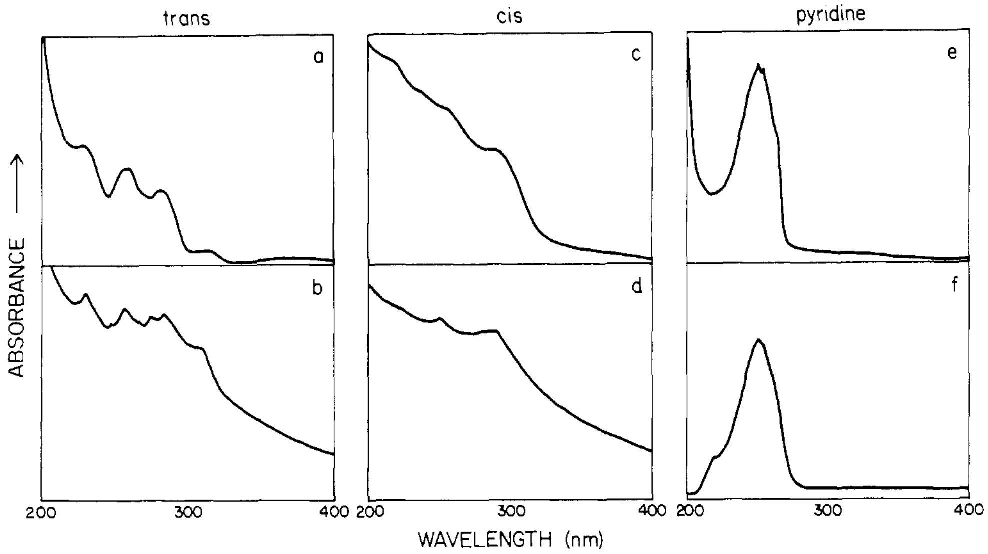

Figure 5. Absorption spectra of (a) trans isomer of $Pt(py)_2Cl_2$ in ethanol at 78 K, (b) trans isomer of $Pt(py)_2Cl_2$ in a KCl pellet at 5 K, (c) cis isomer of $Pt(py)_2Cl_2$ in methylene chloride at 169 K, (d) cis isomer of $Pt(py)_2Cl_2$ in a KCl pellet at 5 K, (e) pyridine in methylene chloride at 169 K, and (f) pyridine in ethanol at 78 K.

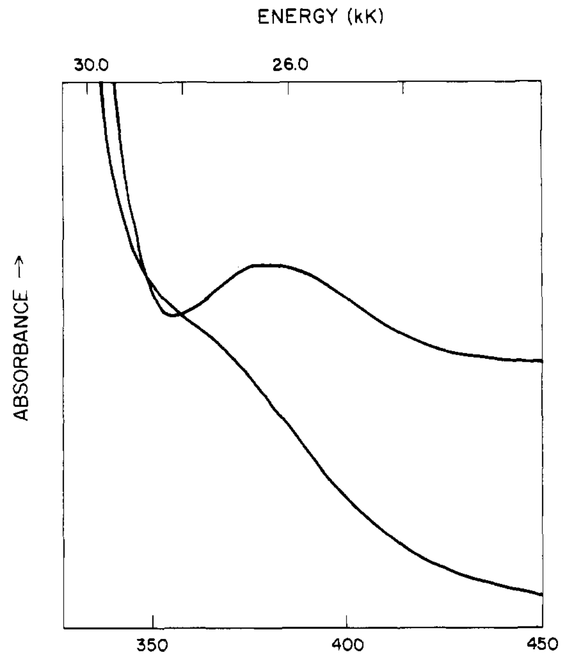

Figure 6. Absorption spectrum and the derivative of the absorption spectrum for *trans*-$Pt(py)_2Cl_2$ in methylene chloride at 325–450 nm showing a weak spin-forbidden electronic transition. The absorption spectrum is the lower curve. The upper derivative curve indicates an absorption maximum is present at about 370 nm.

Table II. Electronic States Arising from One-Electron Excitation to the Lowest Energy Unoccupied π^* Orbitals from the Occupied d Orbitals for *trans*- and *cis*-$Pt(py)_2Cl_2$[a]

	term symbol	
excitation	no spin-orbit coupling	spin–orbit coupling
(a) Trans Isomer (D_{2h} Symmetry)		
$b_{1g}(xy) \rightarrow \pi^*(b_{3u})$	$^1B_{2u}$; $(^3B_{2u})$	B_{2u}; B_{3u}, (A_u), B_{1u}
$b_{2g}(xz) \rightarrow \pi^*(b_{3u})$	$^1B_{1u}$; $(^3B_{1u})$	B_{1u}; (A_u), B_{3u}, B_{2u}
$b_{3g}(yz) \rightarrow \pi^*(b_{3u})$	(^1A_u); (^3A_u)	(A_u); B_{1u}, B_{2u}, B_{3u}
$a_{1g}(z^2) \rightarrow \pi^*(b_{3u})$	$^1B_{3u}$; $(^3B_{3u})$	B_{3u}; B_{2u}, B_{1u}, (A_u)
(b) Cis Isomer (C_{2v} Symmetry)		
$a_1(x^2-y^2) \rightarrow \pi^*(a_1)$	$(^1A_1)$; $(^3A_1)$	(A_1); A_2, B_1, B_2
$a_1(x^2-y^2) \rightarrow \pi^*(b_2)$	$^1B_2$; $(^3B_2)$	B_2; B_1, B_2, (A_1)
$a_2(xz) \rightarrow \pi^*(a_1)$	$^1A_2$; $^3A_2$	A_2; (A_1), B_2, B_1
$a_2(xz) \rightarrow \pi^*(b_2)$	$^1B_1$; $^3B_1$	B_1; B_2, (A_1), A_2
$b_1(yz) \rightarrow \pi^*(a_1)$	$^1B_1$; $^3B_1$	B_1; B_2, (A_1), A_2
$b_1(yz) \rightarrow \pi^*(b_2)$	$^1A_2$; $^3A_2$	A_2; (A_1), B_2, B_1
$a_1(z^2) \rightarrow \pi^*(a_1)$	$(^1A_1)$; $(^3A_1)$	(A_1); A_2, B_1, B_2
$a_1(z^2) \rightarrow \pi^*(b_2)$	$^1B_2$; $^3B_2$	B_2; B_1, B_2, (A_1)

[a] States to which transitions from the $^1A_{1g}$ ground state are forbidden by symmetry are in parentheses. For the D_{2h} point group the electric dipole moment operator transforms as the B_{1u}, B_{2u}, B_{3u} irreducible representations; for the C_{2v} point group $\vec{\mu}$ transforms as the A_1, B_1, B_2 irreducible representations.

cm^{-1}. These are assigned, respectively, to d_{xy}, $d_{xz} \rightarrow \pi^*(b_{3u})$, and $d_{z^2} \rightarrow \pi^*(b_{3u})$ transitions. In making these assignments, we assume crystal field d–d interaction > spin–orbit interaction > interelectron repulsion. The assignments for the cis isomer have been made in a similar way, and the results are given in Table III.

Let us now assign the observed weak transitions. For the cis isomer the observed d–d luminescence maximum for *cis*-$Pt(py)_2Cl_2$ is shifted to the red by 3150 cm^{-1} in comparison to that for *cis*-$Pt(NH_3)_2Cl_2$. If we assume that the energy difference between the lowest energy singlet–triplet d–d absorption maximum and the d–d luminescence maximum is the same for *cis*-$Pt(py)_2Cl_2$ as for *cis*-$Pt(NH_3)_2Cl_2$, then the lowest observed singlet–triplet d–d *cis*-$Pt(py)_2Cl_2$ absorption is predicted to be at 21 500 cm^{-1}. In fact, Textor and Ludwig[9] have observed by diffuse-reflection measurements a band at 22 000 cm^{-1}, which we assign as a d–d spin-forbidden transition. Also, a weak transition at 27 250 cm^{-1} ($\epsilon = 28\ M^{-1}\ cm^{-1}$) has been observed. If the d–d singlet–triplet bands are at the same relative energies in $Pt(py)_2Cl_2$ as in $Pt(NH_2)_2Cl_2$, the 30 500-cm^{-1} amine band corresponds to a band at about 27 300 cm^{-1} for $Pt(py)_2Cl_2$. Thus, the observed band at 27 250 cm^{-1} is assigned as a d–d singlet–triplet transition.

At 43 900 cm^{-1} an additional absorption band occurs for the *trans*-$Pt(py)_2Cl_2$ isomer. From the MO calculations we have carried out, this band is assigned as 5d(Pt) → $6p_z$. All of the assignments are given for our experimental data in Table III.

Conclusions

We have found for the cis isomer of $Pt(py)_2Cl_2$, where py is a π-donor ligand, that the LUMO is a d metal orbital. Also, the cis and trans isomers of $Pt(NH_3)_2Cl_2$, where NH_3 is a σ-bonding ligand, have a d LUMO. These experimental pyridine ligand results are in disagreement with both ours as

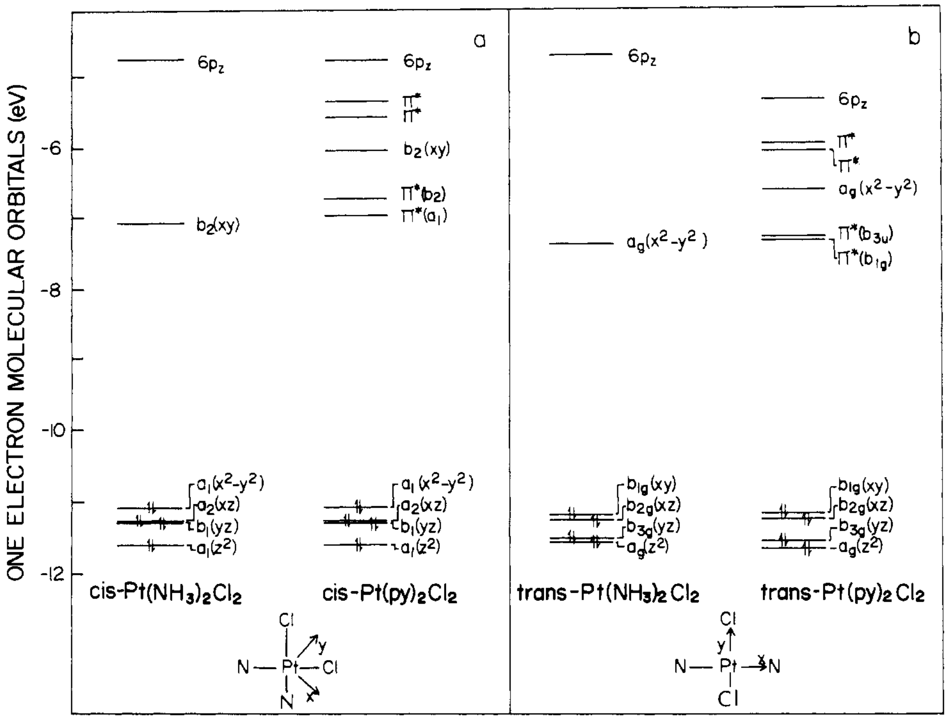

Figure 7. Energy level diagram for the (a) cis and (b) trans isomers of $Pt(py)_2Cl_2$ and $Pt(NH_3)_2Cl_2$ showing the results of a Hückel calculation for these species. Our time-resolved luminescence data for *cis*-$Pt(py)_2Cl_2$ indicates that the d_{xy} orbital is below the pyridine π^* (b_2 and a_1) orbitals in contradiction to the MO predictions. The listed irreducible representations are for the C_{2v} (cis) and D_{2h} (trans) point groups.

Table III. Assignment of the Visible-UV Absorption and MCD Spectra of *cis*- and *trans*-$Pt(py)_2Cl_2$ and Pyridine

energy, cm^{-1} (ϵ, cm^{-1} M^{-1})				
ethanol, 78 K	methylene chloride, 100 K	KCl, 5 K	MCD, $[\Theta]_M$	assignt
		(a) Trans Isomer		
	27 550 (21)			$d_{xy} \rightarrow d_{x^2-y^2}$ ($^3B_{1g}$)
32 300 (3310)	32 600 (3440)	28 700		$d_{xy},d_{xz} \rightarrow \pi^*(b_{3u})$ ($^1B_{1u}$, $^1B_{2u}$)
		29 600		
		31 500		
		31 800		
35 700 (3640)	36 100 (7490)	34 500	$-B$	$n \rightarrow \pi^*$
37 000 (3660)		35 600		
37 600 (9760)	37 300 (8550)	36 900	$-B$	$d_{z^2} \rightarrow \pi^*(b_{3u})$ ($^1B_{3u}$)
		37 900		
38 800 (10 700)	38 500 (8950)		$+B$	$\pi \rightarrow \pi^*$
39 400 (10 900)	39 200 (9580)	39 500		$\pi \rightarrow \pi^*$
40 200 (3840)	40 300 (11 900)	42 200		$\pi \rightarrow \pi^*$
43 900 (6260)				$d \rightarrow p_z$
		(b) Cis Isomer		
	27 250 (28)			$d_{x^2-y^2} \rightarrow d_{xy}$ ($^1B_2$)
		33 300	$+B$	$d_{x^2-y^2} \rightarrow \pi^*$ ($^1B_2$)
35 100 (4900)	34 800 (5150)	34 500	$-B$	$n \rightarrow \pi^*$
		36 400		
38 000 (7500)		38 500		$d_{yz},d_{xz} \rightarrow \pi^*$ ($^1A_2$, $^1B_1$)
39 200 (7870)	39 500 (7870)	39 500	$+B$	$\pi \rightarrow \pi^*$
40 300 (9240)				$\pi \rightarrow \pi^*$
43 500 (10 600)	42 400 (8880)	42 400		$d \rightarrow p_z$
	46 100 (9530)			

well as Ibusuki and Saito's Hückel MO calculations, which predict that the LUMO is a π^* ligand state.

Time-resolved luminescence measurements on the cis isomer of $Pt(py)_2Cl_2$ indicate two luminescence maxima at 600 and 700 nm. Comparison of lifetime data for these two bands with the $Pt(NH_3)_2Cl_2$ luminescence lifetime results indicate that the 600- and 700-nm bands should be assigned to d → π^* and d → d transitions, respectively.

Absorption and MCD spectra of the cis and trans isomers of $Pt(py)_2Cl_2$ and pyridine indicate that the observed absorption maxima correspond to metal d → d, metal–pyridine d → π^*, and pyridine n, $\pi \rightarrow \pi^*$ transitions.

Acknowledgment. We wish to acknowledge the electronics assistance provided by Laurence Lester at the University of Maine. This research was supported by the American Cancer Society.

Registry No. *cis*-$Pt(py)_2Cl_2$, 15227-42-6; *trans*-$Pt(py)_2Cl_2$, 14024-97-6.