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Polarized Single-Crystal Study of the More Intense Quartz-Ultraviolet Absorption Bands of *cis*-Dichloro(ethylenediamine)platinum(II) and Its Palladium(II) Analogue

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The relatively intense quartz-ultraviolet absorption bands of $Pt(en)Cl_2$ and $Pd(en)Cl_2$ have been studied through the application of the techniques of polarized single-crystal specular reflection spectroscopy. Each of these compounds has been found to show a strong out-of-plane absorption that in the crystal is strongly shifted to lower energies from its location in the solution spectrum. A strong analogy has been shown to exist between the out-of-plane absorption of these compounds and other planar d^8 systems that crystallize in relatively closely stacked linear arrays. The strong in-plane bands of these compounds have been associated with ligand-to-metal charge-transfer transitions, and in the case of $Pd(en)Cl_2$ detailed orbital assignments have been suggested.

Introduction

The single-crystal spectra of a wide range of planar d^8 complexes that exhibit unusual solid-state effects have been of continuing interest to this laboratory.[1] Included among these complexes have been a number of systems related to Magnus' green salt (MGS), which is itself composed of stacks of alternating $PtCl_4^{2-}$ and $Pt(NH_3)_4^{2+}$ ions where adjacent ions are separated by 3.25 Å.[2] The strong absorption that occurs in the spectrum of the MGS crystal at 295 nm has been shown to be related to the intense absorptions found in solutions containing $PtCl_4^{2-}$ and $Pt(NH_3)_4^{2+}$ at 216 and 195 nm, respectively.[3-5] The strong perturbation of this absorption band in MGS in comparison to that in solution appears to be related to the relatively close packing within the ionic stacks in MGS compared to that found in, e.g., crystals of K_2PtCl_4 and $Pt(NH_3)_4Cl_2$, where stacking also occurs, but adjacent ions are separated by 4.13[6] and 4.21 Å,[7] respectively, and the crystal spectra much more closely resemble those expected from the solution than is the case for MGS.[5]

cis-Dichloro(ethylenediamine)platinum(II), $Pt(en)Cl_2$, appears to present a situation that is closely analogous to that of MGS. Once again one has a stacked crystal structure, in spite of the fact that one does not here have the mutual attraction of oppositely charged ionic species, with a relatively short intermolecular separation of 3.381 Å in the stacks. It is also possible to prepare a palladium(II) analogue of $Pt(en)Cl_2$ having approximately the same metal–metal spacing as the platinum compound.[8] The effort that has been directed toward the study of the optical and the electrical properties of the Magnus salts[9,10] makes the careful characterization of the crystal absorption spectra of $Pt(en)Cl_2$ of particular interest. Such studies also offer the possibility of providing information concerning the absorptive properties, and thus the electronic structure, of these complexes as isolated entities.

Martin et al. have recently reported polarized-crystal absorption spectra for $Pt(en)Cl_2$[11,12] and $Pd(en)Cl_2$.[13] Due to crystal opacity these studies were limited for $Pt(en)Cl_2$ to energies below about 31×10^3 cm^{-1} for radiation polarized parallel to the stacking direction and 43×10^3 cm^{-1} for radiation polarized perpendicular to the stacking direction. For $Pd(en)Cl_2$ the corresponding limit was about 33×10^3 cm^{-1} for both polarizations. In the work reported here the techniques of specular reflection spectroscopy,[1,3,5,14] where the effectiveness of the approach increases with increasing crystal absorption, have been used to characterize the strongly allowed bands that occur in the quartz-ultraviolet spectra of both $Pt(en)Cl_2$ and $Pd(en)Cl_2$.

Table I. Single-Crystal Reflection Data for $Pt(en)Cl_2$ and $Pd(en)Cl_2$

compd	cryst direcn	λ_{max}, nm	$10^{-3}\nu_{max}$, cm^{-1}	R_{max}, %
$Pt(en)Cl_2$	*c*	282	35.4	51.3
	a	221	45.3	15.5
$Pd(en)Cl_2$	*c*	223	44.8	47.0
	a	272	36.8	18.3
	a	222	45.0	27.8
	$[1\bar{1}0]$	224	44.5	24.2

Experimental Section

$Pt(en)Cl_2$ was prepared by the method of Basolo et al.,[15] and crystals suitable for spectral study were grown by slow cooling of hot saturated solutions of $Pt(en)Cl_2$ in 0.05–0.10 M HCl. Crystals from some of the same crops that provided crystals for the spectral work yielded the following elemental analysis. Anal. Calcd for $Pt(en)Cl_2$, $PtC_2N_2H_8Cl_2$: C, 7.37; H, 2.47; N, 8.59; Cl, 21.74. Found: C, 7.48; H, 2.58; N, 8.63; Cl, 21.53. Crystals grown from dilute (0.03–0.30 M) KCl showed, in terms of the axis choice of Iball et al.,[16] (010) as a well-developed face and were used for the study of (010).

$Pd(en)Cl_2$ was prepared by the method of McCormick et al.,[17] and crystals for spectral study were grown from 0.02–0.03 M KCl solutions. Anal. Calcd for $Pd(en)Cl_2$, $PdC_2N_2H_8Cl_2$: C, 10.12; H, 3.40; N, 11.80; Cl, 29.87. Found: C, 10.36; H, 3.52; N, 11.96; Cl, 29.59. The apparatus and methods used to obtain the reflection spectra reported here and the procedures used to transform these spectra to obtain absorption spectra have been reported elsewhere.[14,18]

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(2) Atoji, M.; Richardson, J. W.; Rundle, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3017.
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(16) Throughout this paper the choice of *a* and *b* axes specified by Iball et al.[8] will be used. (The *a* and *b* axes of Martin et al.[11-13] are interchanged relative to those of ref 8.)
(17) McCormick, B. J.; Jaynes, E. N., Jr.; Kaplan, R. I. *Inorg. Synth.* **1972**, *13*, 216.

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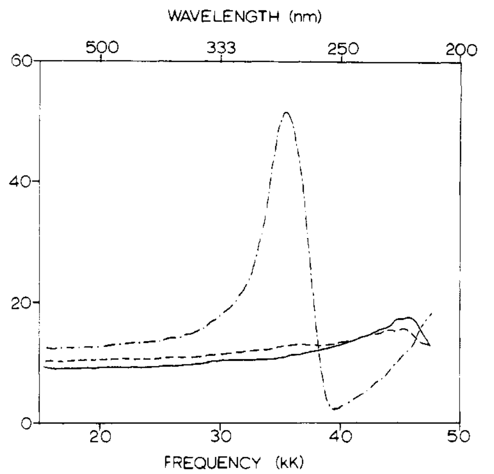

Figure 1. Polarized single-crystal reflection spectra for $Pt(en)Cl_2$ obtained with incident radiation whose electric vector vibrates parallel to *c* (–•–•), parallel to *a* (- - -), and parallel to the direction in (110) that is perpendicular to *c* (the $[1\bar{1}0]$ direction, hereafter) (—).

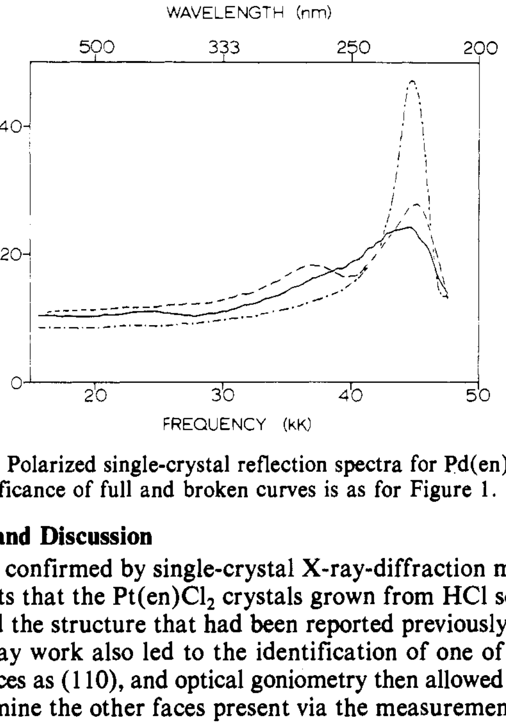

Figure 2. Polarized single-crystal reflection spectra for $Pd(en)Cl_2$. The significance of full and broken curves is as for Figure 1.

Results and Discussion

It was confirmed by single-crystal X-ray-diffraction measurements that the $Pt(en)Cl_2$ crystals grown from HCl solutions had the structure that had been reported previously.[8,12] The X-ray work also led to the identification of one of the major faces as (110), and optical goniometry then allowed one to determine the other faces present via the measurement of interfacial angles. Face identifications for $Pt(en)Cl_2$ grown from KCl solutions and for $Pd(En)Cl_2$ were made solely on the basis of optical goniometry. For both compounds the faces studied in this work were thus shown to be (110) and (010)[16] or faces optically equivalent to them such as, for instance, $(1\bar{1}0)$.

Both $Pt(en)Cl_2$ and $Pd(en)Cl_2$ form crystals belonging to the $C222_1$ space group of the orthorhombic system.[8,12] The crystals are needles elongated along *c* in which the complexes are perpendicular to *c*, and the metal atoms form chainlike arrays parallel to *c* with a metal separation of 3.381 Å in the platinum complex and 3.368 Å in the palladium. (See Figure 1 of ref 12 and Figure 1 of ref 13.)

The optical principal directions for the (110) and (010) lateral faces of the $Pt(en)Cl_2$ and $Pd(en)Cl_2$ crystals are determined by the orthorhombic unit-cell symmetry to be the *c* axis and the direction in the face in question perpendicular to the *c* axis. Reflection spectra obtained with the electric vector of the incident light vibrating parallel to these directions are reported in Figures 1 and 2 and the spectral parameters for the observed reflection bands summarized in Table I. It will be noted that weak reflection maxima that would require considerable additional study to ensure that they are not artifacts have been omitted from Table I.

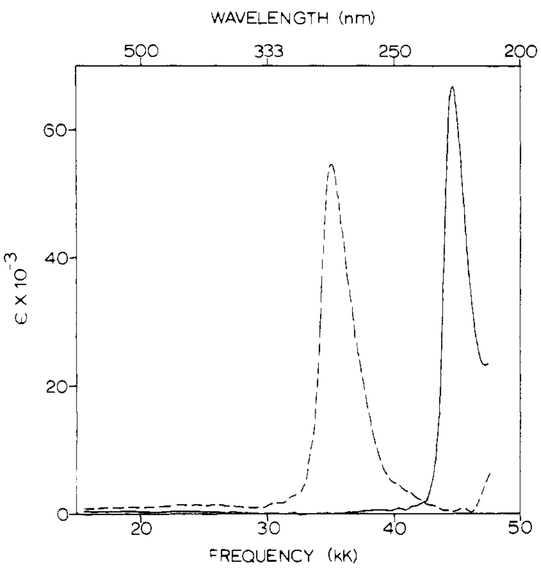

Figure 3. Absorption spectra obtained via the Kramers–Kronig transformation of the reflection spectra shown for the *c* crystallographic direction in Figures 1 and 2: (—) $Pd(en)Cl_2$; (- - -) $Pt(en)Cl_2$. Spectra are reported in terms of crystal ε values (see footnote *a* of Table II).

Table II. Single-Crystal Absorption Data for $Pt(en)Cl_2$ and $Pd(en)Cl_2$

compd	cryst direcn	λ_{max}, nm	$10^{-3} \times \nu_{max}$, cm^{-1}	$10^{-3} \times \epsilon_{max}$, cm^{-1} M^{-1} [a]	$\lvert q \rvert^2$, $Å^2$ [b]
$Pt(en)Cl_2$	*c*	285	35.1	55.1	0.64
$Pd(en)Cl_2$	*c*	224	44.6	62.9	0.55
	a	257	38.9	9.3	0.15
	a	220	45.5	35.8	0.53
	$[1\bar{1}0]$	223	44.9	30.9	
	b[c]	225	44.5	29.4	0.69

[a] Crystal molar extinction coefficients are reported here and for comparison to solution values should be divided by 3. (See ref 5.) [b] The approach used to obtain the transition-moment-squared values is discussed in ref 5. [c] The *b* spectrum was calculated from the *a* and $[1\bar{1}0]$ spectra (see text).

The reflection spectra reported in Figures 1 and 2 are the average of as many as ten individual determinations in the ultraviolet portion of the spectrum and, in general, two in the less critical visible region. All spectra for which Kramers–Kronig transforms are reported contain the average of at least three ultraviolet spectra.

The assignment of Cartesian molecular axes corresponds here to that of Martin et al.[12,13] Hence, the molecular *z* axis is taken as out of plane, *y* is taken as the in-plane 2-fold axis that bisects the Cl–Pt–Cl or the Cl–Pd–Cl angle, and *x* is taken as the remaining in-plane axis. Transitions occurring in the *c* crystal spectra thus have *z* (or out-of-plane) molecular polarization, and those with *a* crystal polarization have *y* molecular polarization. $[1\bar{1}0]$, the direction perpendicular to *c* on (110), will show mixed molecular polarization with *x*-polarized transitions appearing with 70% of their full intensity and *y*-polarized transitions appearing with 30% of their full intensity.

Out-of-Plane Transitions. Figure 3 presents the absorption spectra obtained through the application of the Kramers–Kronig transformation to the out-of-plane spectra of Figures

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(18) Parkhurst, L. J.; Anex, B. G. *J. Chem. Phys.* **1966**, *45*, 862.

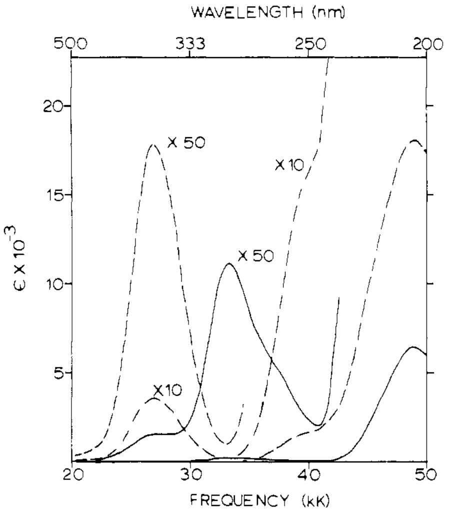

Figure 4. Solution absorption spectra for Pt(en)Cl_2 (—) and Pd(en)Cl_2 (- - -). These spectra were obtained in solutions containing excess chloride ion to suppress aquation of the complexes.

Table III. Comparison of Single-Crystal Absorption Parameters of Pt(en)Cl_2 and Magnus' Green Salt (MGS)

	$10^{-3}\nu_{max}$, cm^{-1}	$10^{-3}\epsilon_{max}$, cm^{-1} M^{-1} [b]	$\lvert q\rvert^2$, $Å^2$
MGS[a]	33.9	16.1	0.75
Pt(en)Cl_2	35.1	18.4	0.64

[a] From ref 4. [b] Solution equivalent.

1 and 2. The various parameters that characterize the absorption spectra of Figure 3 are summarized in Table II. The transition-moment lengths ($\lvert q\rvert^2$'s) reported in Table II are obtained through appropriate graphical integration of the corresponding absorption bands.[5] The actual $\lvert q\rvert^2$ values reported are averages of those obtained under various assumptions concerning such matters as base-line corrections and resolution of overlapping bands. Base-line uncertainties introduce considerable uncertainty into the $\lvert q\rvert^2$ values (and ϵ_{max} values) reported for bands near the high-energy limits of measurement such as the Pd(en)Cl_2 band of Figure 3.

Figures 1 and 3 indicate a strong out-of-plane band in the Pt(en)Cl_2 absorption spectrum at about 35 000 cm^{-1}. This peak has a solution-equivalent ϵ_{max} value of 18.4 × 10^3 cm^{-1} M^{-1}, while the solution spectrum shown in Figure 4 possesses no absorption with an extinction coefficient greater than a few hundred cm^{-1} M^{-1} at energies below 42 × 10^3 cm^{-1}. At the same time, much of the intensity present in the high-energy region of the solution spectrum does not appear to be present at corresponding energies in the crystal spectra. It is thus reasonable to assume that the situation here is analogous to that observed for MGS, where, as noted in the Introduction, strong absorption bands that occur in the component spectra near the high-energy edge of the quartz-ultraviolet region shift dramatically to the red region in the mixed salt. The analogy between MGS and Pt(en)Cl_2 becomes even clearer from an examination of Table III, where the spectral parameters for the corresponding bands in these systems are seen to be remarkably similar. The fact that the MGS peak is shifted more to the red region and is more intense than that of Pt(en)Cl_2 correlates with the shorter intercomplex spacing in MGS (3.25 Å vs. 3.38 Å in Pt(en)Cl_2).[2,3,8,12]

The high-energy solution absorption spectrum of Pt(en)Cl_2 is seen in Figure 4 to be incompletely determined. It is clear, however, if one accepts the correlation between this absorption and the 35 000-cm^{-1} crystal band, that there has been an increase in intensity in the solid. The solution ϵ_{max} is 6.6 × 10^3 cm^{-1} M^{-1}, while that of the crystal absorption is 18.4 × 10^3 cm^{-1} M^{-1}. Moreover, Martin et al.[12] estimate a solution oscillator strength of 0.20. This corresponds to a $\lvert q\rvert^2$ value of 0.38 $Å^2$ and, in combination with data of Table II, implies a 1.7-fold increase of intensity in the crystal. MGS itself has been found to have a $\lvert q\rvert^2$ value about 2.8 times as great as that which is thought to be associated with the corresponding solution absorption in $PtCl_4^{2-}$.[4] The intensity increases noted for Pt(en)Cl_2 and MGS are in reasonably good agreement in light of the approximations involved in the determination of all the $\lvert q\rvert^2$ values involved, the closer metal–metal distance in MGS, and the fact that, as noted in the following section, the high-energy solution spectrum of Pt(en)Cl_2 likely contains some in-plane absorption. It appears reasonable, then, to associate the 35 000-cm^{-1} band of Pt(en)Cl_2 with the 34 000-cm^{-1} peak of MGS and, in accord with the previous MGS assignment,[1,3,5] with a metal-localized $5d_{z^2} \rightarrow 6p_z$ transition.

Pd(en)Cl_2 is also seen in Figure 3 to show a strong out-of-plane absorption, which occurs at 44.6 × 10^3 cm^{-1}. It will be noted that this compound has considerable intensity in its solution spectrum at the energies where the out-of-plane crystal band occurs. As will be discussed in the following section, however, sufficient in-plane crystal absorption is observed in this region to account for the high-energy solution absorption of this compound. The most reasonable assumption to make, especially in light of the similar absorptions seen in analogous crystals containing Pt(II) and Pd(II) complexes,[19,20] would thus appear to be that the Pd(en)Cl_2 out-of-plane transition is also related to a metal-confined d → p transition and has been shifted in a manner analogous to that observed for Pt(en)Cl_2. If the solid-state shift for the palladium system is of a magnitude similar to that observed for Pt(en)Cl_2, the d → p transition in Pd(en)Cl_2 would be estimated to occur at about 58 000 cm^{-1} (170 nm) in solution.

There is a strong similarity between the comparative spectral properties of Pt(en)Cl_2 and Pd(en)Cl_2 and those of other platinum–palladium pairs of planar d^8 complexes that have been reported.[19,20] For instance, the separation between the strong out-of-plane peaks observed for the compounds studied here is 9.5 × 10^3 cm^{-1}, an interval that is comparable to that observed for MGS and its palladium analogue[19] and for $Ba[Pt(CN)_4]\cdot 4H_2O$ and $Ba[Pd(CN)_4]\cdot 4H_2O$.[20] It will be noted the Pt(en)Cl_2 crystals contain stacks of neutral species, all of which are the same, the Magnus salts consist of stacks of alternating positive and negative ionic species with quite different ligands, and the cyanides contain anionic stacks in which the complexes contain ligand unsaturation. The present study thus provides further support for a suggestion made previously[1,20] that the striking crystal perturbations noted in the spectra of a wide variety of d^8 complexes very likely have a similar origin.

In-Plane Transitions. The experimental situation with respect to the in-plane spectra of Pd(en)Cl_2 is relatively unambiguous. These transitions will thus be discussed first in this section, and the conclusions drawn from them will be used in a brief discussion of the Pt(en)Cl_2 in-plane data.

It will be observed that the in-plane Pd(en)Cl_2 spectra of Figures 2 and 5 show three strong absorptions, for which the spectral parameters are summarized in Tables I and II. As noted previously, the *y*, or 2-fold, molecular axis lies parallel to *a*. The two bands appearing in the *a* spectrum thus have *y* molecular polarization, and their spectral parameters may be determined directly from the experimental curves. The $[1\bar{1}0]$ curve is predominantly (70%) *x*, and thus the peak that occurs in this direction clearly has *x* polarization. The spectral data listed in Table II for the experimentally unobserved *b*

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(19) Anex, B. G.; Foster, S. I.; Fucaloro, A. F. *Chem. Phys. Lett.* **1973**, *18*, 126.

(20) Anex, B. G.; Musselman, R. L. *J. Phys. Chem.* **1980**, *84*, 883.

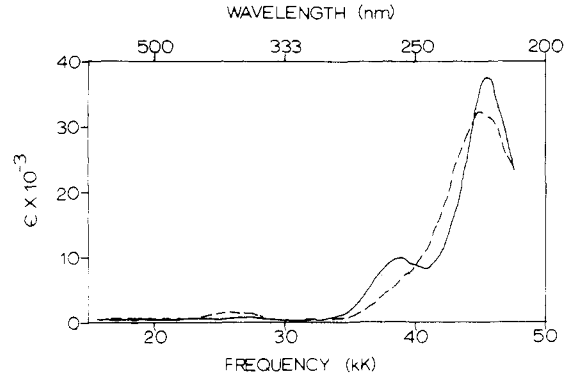

Figure 5. Absorption spectra obtained via the Kramers–Kronig transformation of the in-plane reflection spectra of Pd(en)Cl_2: (—) *a* spectrum; (- - -) [1$\bar{1}$0] spectrum.

crystallographic direction, which will correspond to those for the *x*-polarized molecular transitions, were obtained by subtracting three-tenths of the *a* absorption curve from the [1$\bar{1}$0] curve and dividing the result by 0.7. Integration of the entire high-energy solution absorption band of Pd(en)Cl_2 yields an overall $|q|^2$ value of 1.26 Å^2. The sum of $|q|^2$ values listed in Table III for three in-plane crystal transitions found in this region is 1.37 Å^2. This rather good agreement indicates that, as noted previously, the in-plane crystal absorption bands account for the observed high-energy solution intensity and points to the molecular origin of the strong out-of-plane crystal absorption being in the vacuum-ultraviolet region.

The strong in-plane absorption bands that are observed at 35.7×10^3 and 44.9×10^3 cm^{-1} in solutions containing the $PdCl_4^{2-}$ ion have been assigned to ligand-to-metal (L → M) transitions.[5,21] It would thus seem reasonable to make a similar assignment for the three strong in-plane bands observed here. The fact that the Pd(en)Cl_2 spectra show three such bands and only two are observed for the $PdCl_4^{2-}$ ion is not unexpected in view of the lower symmetry (C_{2v})[22] of Pd(en)Cl_2 compared to that (D_{4h}) of the $PdCl_4^{2-}$ ion.

In considering the detailed assignment of the Pd(en)Cl_2 absorptions in terms of orbital transitions, the conventions of Gray and Ballhausen[21d] regarding the phases of, and nomenclature for, the 2p chlorine orbitals have been adopted. Hence, a chlorine 2p orbital involved in σ bonding with the Pd atom will be designated σ, the other in-plane 2p orbital on each chlorine will be designated π_h, and the out-of-plane 2p orbital on each chlorine will be designated π_v. The symmetry-adapted linear combinations of the chlorine 2p orbitals and their symmetries in C_{2v} are shown in Chart I.

Chart I

(1) $C_1(\pi_{1v} + \pi_{2v})$ b_1
(2) $C_2(\pi_{1v} - \pi_{2v})$ a_2
(3) $C_3(\pi_{1h} + \pi_{2h})$ b_2
(4) $C_4(\pi_{1h} - \pi_{2h})$ a_1
(5) $C_5(\sigma_1 + \sigma_2)$ a_1
(6) $C_6(\sigma_1 - \sigma_2)$ b_2

Table IV lists the symmetries of the excited states generated by the transfer of an electron from functions 1 through 6 to the empty $5d_{xy}$ Pd orbital, which will itself have b_2 symmetry in C_{2v}. Included in Table IV is the polarization that is anticipated for a transition from the A_1 ground state of Pd(en)Cl_2 to each excited state considered. It will be noted that there are four allowed in-plane transitions listed in Table IV, two polarized *x* and two polarized *y*.

Table IV. Symmetries of the Anticipated Low-Energy L → M Charge-Transfer Transitions and Their Assignments to Observed Pd(en)Cl_2 Absorption Bands

transition	excited-state symm	polarizn	assignt (band position × 10^{-3}), cm^{-1}
(1) → d_{xy}	A_2	forbidden	
(2) → d_{xy}	B_1	*z*	
(3) → d_{xy}	A_1	*y*	38.9
(4) → d_{xy}	B_2	*x*	44.5 (?)
(5) → d_{xy}	B_2	*x*	44.5 (?)
(6) → d_{xy}	A_1	*y*	45.5

The lower energy of the two strong in-plane quartz-ultraviolet transitions observed for $PdCl_4^{2-}$ is generally assigned as L → M and as originating essentially from the chlorine π_h orbitals.[21] A similar assignment for Pd(en)Cl_2 would lead to the association of (3) → d_{xy} transition with the *y*-polarized 38.9×10^3 cm^{-1} band. One would then be led to associate the higher energy *y*-polarized band with the (6) → d_{xy} transition, whose σ-orbital origin would be the same as that assigned to the higher energy $PdCl_4^{2-}$ L → M transition. Such assignments for the 38.9×10^3 and 45.5×10^3 cm^{-1} Pd(en)Cl_2 bands are also consistent with Jørgensen's observation[21b] in connection with his discussion of the $PdCl_4^{2-}$ spectrum that one expects L → M charge-transfer transitions involving σ ligand orbitals to be more intense than those involving π ligand orbitals.

Only one band of *x* polarization is observed here, while Table IV predicts two. The interligand antibonding character of (3) with respect to (4) and the similar relationship of (6) to (5) would suggest assigning the 44.5×10^3 cm^{-1} band of Pd(en)Cl_2 to (4) → d_{xy} and the placement of (5) → d_{xy} at energies higher than those studied here. It will be noted, however, that the *x*-polarized band is the most intense of the three in-plane crystal bands, and on this basis one would be led to associate it with the L(σ) → M transition (5) → d_{xy}. In Table IV, therefore, the 44.5×10^3 cm^{-1} band has been tentatively assigned as containing both of the expected *x*-polarized transitions. Such an assignment implies that (5) lies above (6) in energy, in spite of the interligand bonding character of the former relative to the latter. It may be observed in this connection that (6) is favorably oriented and has the proper symmetry for interaction with the metal d_{xy} orbital. It would not be unreasonable for such interaction, in concert with others, such as that between (3) and (6) to cause (6) to fall below (5) in energy.[23]

Table IV predicts the existence of an out-of-plane polarized transition originating in π_v chlorine orbitals that has not been assigned here. A similar transition is predicted for $PdCl_4^{2-}$ but is not observed in the single-crystal specular reflection spectra of K_2PdCl_4.[5] Rush et al.,[21c] however, have observed in direct crystal absorption studies of K_2PdCl_4 a weak out-of-plane absorption that they associated with the L(π_v) → M transition. The ϵ value reported for this absorption was 388 M^{-1} cm^{-1}, a value considerably lower than that which one expects to be detected in room-temperature specular reflectance studies. Hence, it is not surprising that the analogous

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(22) Although Pd(en)Cl_2 rigorously possesses C_2 molecular symmetry, it will be discussed here, as has been done for Pt(en)Cl_2 and Pd(en)Cl_2 by other workers,[11-13] in terms of local C_{2v} symmetry around the palladium atom.

(23) In a case such as this, where the transitions involved are fairly close in energy, the fact that spectroscopic measurements strictly speaking give information on state, not orbital, energies may also be a factor to be considered in explaining an apparent reversal of orbital energies.

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.

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

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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 $\rightarrow$ π^*, 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 $\rightarrow$ π^* 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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