POLARIZED CRYSTAL ABSORPTION SPECTRA FOR DIBROMO-
(ETHYLENEDIAMINE) PLATINUM(II)

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Polarized Crystal Absorption Spectra for
dibromo(ethylenediamine)platinum(II)

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The polarized electronic absorption spectra of dibromo(ethylenediamine)platinum(II) have been recorded for crystals at 300°K, 77°K and 15°K. The orthorhombic structure of the complex makes it possible to record the absorption in both c and b polarizations. The square planar molecules stack in chains only 3.50Å apart in the c direction. The crystal spectra indicate unusual crystal effects which are apparently a result of the short Pt-Pt distance. A one-dimensional exciton theory is employed which accounts for the observed phenomena. A dipole allowed transition in the c polarization, $d_{xy}^* \leftarrow L(\pi)$, has been shifted from the 44,000-50,000 cm^{-1} region in the solution to 36,700 cm^{-1} in the crystal. In b polarization, the temperature dependence of a peak at 33,500 cm^{-1} indicates some dipole allowed character. This transition has been assigned to an ionized exciton state which is an excitation of an electron from the d_{xz} orbital to the d_{xy}^* orbital on the adjacent molecule.

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1. INTRODUCTION

The purpose of this research has been to study the single crystal polarized absorption spectra of dibromo(ethylenediamine)platinum(II). This system exhibits large crystal effects on the electronic absorption spectra of a square planar d^8 complex. Similar to the results in the chloride system, evidence was obtained for the existence of an unusually large red shift of a Frenkel exciton and the presence of an ionized exciton state.

As a basis, a summary of the spectra and transition assignments for K_2PtCl_4 will be presented. The spectra of potassium trichloroammineplatinate(II)monohydrate, also known as monoammine or Cossa's salt, will be briefly presented in terms of the perturbation of the $PtCl_4^{2-}$ spectrum. The spectra of dichloro(ethylenediamine)platinum(II) will be thoroughly reviewed since the results can be directly related to the bromide system.

The assignments of the transitions and the ordering of the d-orbitals in potassium tetrachloroplatinate, K_2PtCl_4 , first appeared about 1958 in a paper by Chatt, Gamlen and Orgel(1). Since then much experimental and theoretical work has been done. Chatt, Gamlen and Orgel based their results on the solution spectrum of $PtCl_4^{2-}$, Figure 1, and a series of other chloroamine complexes. They assigned the low energy transitions at $21,000\text{ cm}^{-1}$ and $17,000\text{ cm}^{-1}$ as spin forbidden, singlet $\rightarrow$ triplet, transitions. These transitions were observed because of the large spin-orbit coupling of the platinum atom. The two peaks at $25,400\text{ cm}^{-1}$ and $30,300\text{ cm}^{-1}$ were assigned to the one-electron

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Figure 1. Solution spectrum of K_2PtCl_4

spin allowed transitions, $d_{x^2-y^2}^* \leftarrow d_{xy}$ and $d_{x^2-y^2}^* \leftarrow d_{xz,yz}$, respectively. The fourth $d \leftarrow d$ transition, $d_{x^2-y^2}^* \leftarrow d_{z^2}$, was assigned to the shoulder at $37,900 \text{ cm}^{-1}$.

The high intensity of the bands at $43,400$ and $46,400 \text{ cm}^{-1}$ indicates that they are strongly dipole allowed. Chatt, Gamlen and Orgel (1) assigned the $46,400 \text{ cm}^{-1}$ peak to an allowed $p \leftarrow d$ transition, presumably $p_z \leftarrow d_{xz,yz}$. They did not report the $43,400 \text{ cm}^{-1}$ band. Cotton and Harris (2) using a semi-empirical molecular orbital treatment support this assignment. McCaffery, Schatz and Stephens (3) also support this assignment using magnetic circular dichroism as a basis. However, Jorgensen (4) and Gray and Ballhausen (5) prefer a $d_{x^2-y^2}^* \leftarrow \pi$ -Ligand assignment.

Much experimental and theoretical work followed Chatt, Gamlen and Orgel's ordering of the d-orbitals. Theoretical studies could be easily applied to the PtCl_4^{2-} ion because of its high D_{4h} symmetry. Fenske, Martin and Ruedenberg (6) took a ligand field approach including electron-electron repulsions and spin-orbit coupling. Their results were not consistent with Chatt, Gamlen and Orgel. Basch and Gray (7) and Cotton and Harris (2) employed a semi-empirical molecular orbital treatment in their consideration of PtCl_4^{2-} . Their results did not yield definite assignments either.

Experimentally, several techniques in addition to the solution spectrum study (1) have been applied to the PtCl_4^{2-} problem. They include polarized single crystal absorption spectra at various temperatures (8-10), powder reflectance spectra (10), magnetic circular

dichroism (3,11) and low temperature solution spectrum in a frozen organic solvent (12). The high symmetry, D_{4h} , of the complex and the eclipsed stacking of the $PtCl_4^{2-}$ ions in the crystal provide an excellent system for single crystal polarized spectral work. The structure of K_2PtCl_4 was determined by Dickinson (13), later refined by Staritzky (14) and more recently by Mais et al. (15). The planar $PtCl_4^{2-}$ molecules stack in chains along the z or c axis. For this discussion, the x and y axes will be directed along the Pt-Cl bonds. The polarized crystal spectra at room temperature and $15^\circ K$ are shown in Figure 2. These spectra show that all the d-d transitions result from vibronic coupling. Since $PtCl_4^{2-}$ has a center of inversion, all d-d transitions are Laporte forbidden. However, molecular vibrations destroy this center of symmetry, that is, the Laporte forbidden transitions borrow intensity from allowed transitions in the same polarization. The intensity of a vibronic absorption band is dependent on the amount that the vibration destroys the high symmetry of the complex, that is, the magnitude of the vibration. Therefore, the intensity of a band would be expected to decrease when the amount of molecular vibration is decreased. This is seen in Figure 2 where the intensity of the d-d bands decreases upon going to $15^\circ K$. At this low temperature, the molecular motion is greatly reduced resulting in a decrease in the intensity of the absorption.

The band assignments for the polarized single crystal spectra of Martin and coworkers (16,17) agree with solution spectra assignments allowing for slight shifts in energy. The assignments of Martin et al.

Figure 2. Polarized crystal absorption spectra of K_2PtCl_4 at 300° and $15^\circ K$

which appear in Table 1, are generally accepted to be correct.

Evidently, the solid state spectrum of K_2PtCl_4 results from oriented $PtCl_4^{2-}$ ions which are isolated sufficiently so there are no large intensity changes or energy shifts from crystal effects. The logic for the assignments of Martin et al. is as follows. The $d_{x^2-y^2}^*$ orbital appears highest in energy, Figure 5, because it is the lowest unfilled orbital, an antibonding orbital. The lowest energy singlet transition, $^1A_{2g} \leftarrow ^1A_{1g}(d_{x^2-y^2}^* \leftarrow d_{xy})$, should be only xy polarized. It was assigned to the $26,300\text{ cm}^{-1}$ peak ($25,400\text{ cm}^{-1}$ in solution). The next singlet transition, $^1E_g \leftarrow ^1A_{1g}(d_{x^2-y^2}^* \leftarrow d_{xz,yz})$, is both z and xy polarized. In addition, magnetic circular dichroism in solution (3,11) indicated that the $30,300\text{ cm}^{-1}$ transition terminated in a degenerate excited state. Therefore, the $28,500\text{ cm}^{-1}$ band in the xy polarization and the $29,300\text{ cm}^{-1}$ band in the z polarization were assigned to the $^1E_g \leftarrow ^1A_{1g}$ transition. The two broad bands at $21,000\text{ cm}^{-1}$ and $17,500\text{ cm}^{-1}$ were assigned as the triplet transitions corresponding to the above singlet transitions, respectively.

The next band, $37,900\text{ cm}^{-1}$ in the solution spectrum, has been assigned to the $^1B_{2g} \leftarrow ^1A_{1g}(d_{x^2-y^2}^* \leftarrow d_{z^2})$ transition. Much of the work on this complex was done in order to determine this assignment.

Qualitatively, Basch and Gray (7) and Cotton and Harris (2) support this assignment. A triplet state transition corresponding to this transition lies at $23,800\text{ cm}^{-1}$ in both polarizations of the crystal spectra.

The polarized crystal spectra of potassium trichloroammineplatinate-(II)monohydrate, Cossa's salt, was studied by Fanwick (18).

Table 1. Spectral assignments for K_2PtCl_4 and $KPt(NH_3)_3Cl_3 \cdot H_2O$ (1,16-20).
(Energies in $cm^{-1} \times 10^{-3}$, molar absorptances in parentheses)

K_2PtCl_4	${}^3A_{2g}(d_{xy})$	${}^3E_g(d_{xz},yz)$	${}^3B_{1g}(d_{z^2})$	${}^1A_{2g}(d_{xy})$	${}^1E_g(d_{xz},yz)$	${}^1B_{1g}(d_{z^2})$		
solution	17.0(2?)	21.0(15)	--	25.4(57)	30.3(62)	37.9(250)		
x,y(a)								
300°K	--	20.4(18)	23.4(9?)	25.7(62)	28.7(74)	--		
15°K	18.0(2)	20.9(8.7)	24.0(7.1)	26.3(28)	29.2(37)	--		
z(c)								
300°K	--	20.2(20)	23.7(5)	--	29.3(101)	--		
15°K	17.0-19.0(1)	20.6(10)	24.1(3)	--	29.8(55)	--		
$KPt(NH_3)Cl_3$	${}^3B_2(d_{xy})$	${}^3A_2(d_{xz})$	${}^3B_1(d_{yz})$	${}^3A_1(d_{z^2})$	${}^1B_2(d_{xy})$	${}^1A_2(d_{xz})$	${}^1B_1(d_{yz})$	${}^1A_1(d_{z^2})$
solution	20.8(6?)	24.0(20.5)	--	28.9(109)	33.4(71)			--
x(c)								
300°K	20.2(27)	23.3(52)	--	28.8(303)	32.1(108)	--	--	--
15°K	20.0(22)	23.3(41)	--	29.4(334)	32.5(47)	--	--	--
z(a)								
300°K	--	23.9(23)	28.7(5)	--	--	33.0(106)	--	--
15°K	--	24.3(11)	29.2(10)	--	--	33.7(59)	--	--

It represented a complex similar to PtCl_4^{2-} but with lower symmetry, C_{2v} , having no center of inversion. Cossa's salt, like K_2PtCl_4 , had a crystal structure very suitable to polarized crystal spectroscopy. The $\text{Pt}(\text{NH}_3)\text{Cl}_3^-$ ions stack in columns along the a axis (21), Figure 3. The crystals grew with 010 faces, so that, light polarized along the c and a crystal axes gave pure molecular x and z polarizations, respectively.

The solution spectrum (18-20), Figure 4, can be directly related to the K_2PtCl_4 solution spectrum. The results appear in Table 1. Figure 5 shows the correlation between D_{4h} and C_{2v} assignments. Generally, the bands are at slightly higher energy than in K_2PtCl_4 . This shift is consistent with the relative positions of chloride and ammonia in the spectrochemical series of Fajans (22) and Tsuchida (23). The somewhat higher intensities of the $\text{KPt}(\text{NH}_3)\text{Cl}_3 \cdot \text{H}_2\text{O}$ spin-allowed bands is due to the nonzero transition dipole moments. These transition moments contribute some intensity to the spin-allowed bands because of the lower symmetry, C_{2v} , of the complex.

The crystal spectra (18-20), Figure 6, are consistent with the C_{2v} symmetry of the $\text{Pt}(\text{NH}_3)\text{Cl}_3^-$ ions. The peak at $28,900 \text{ cm}^{-1}$ in the solution spectrum corresponds to the $28,800 \text{ cm}^{-1}$ band at 300°K in the c or x polarized crystal spectrum. This band is extremely small in the a or z polarization. This absorption has been assigned to $^1B_2 \leftarrow ^1A_1$ ($d_{x^2-y^2}^* \leftarrow d_{xy}$) transition. This transition is both a ligand field and a vibronic excitation which is completely forbidden in the z polarization. Since it is a vibronic excitation, it is expected to

Figure 3. Crystal structure of $\text{KPt}(\text{NH}_3)\text{Cl}_3 \cdot \text{H}_2\text{O}$. The unit cell with the solid atoms at $\underline{a}=0$ and the dashed atoms at $\underline{a}=\frac{1}{2}$

Figure 4. Solution spectrum of $\text{KPt}(\text{NH}_3)\text{Cl}_3 \cdot \text{H}_2\text{O}$

Figure 5. Ordering of the d orbitals for PtCl_4^{2-} and $\text{Pt}(\text{NH}_3)\text{Cl}_3^-$ with symmetry designations for D_{4h} and C_{2v} .

Figure 6. Polarized crystal spectra of $\text{KPt}(\text{NH}_3)\text{Cl}_3 \cdot \text{H}_2\text{O}$ at 300° and 15°K

decrease in width and height at low temperatures. However, a ligand field excitation is expected to increase in height as it becomes narrower at cryogenic temperatures (12). Since the height of this band barely changes from 300°K to 15°K, the ligand field and vibronic contributions are almost balanced in this excitation.

In the other polarization, a-z, there is a very weak band between 28,700 and 29,000 cm^{-1} . The transition in the c-x polarization in this region is completely forbidden in the a-z polarization, unless, the C_{2v} symmetry is broken by the site symmetry. In the K_2PtCl_4 crystal spectrum, a weak spin-forbidden transition, $d_{x^2-y^2}^* \leftarrow d_{z^2}$, appears in the same region as the $d_{x^2-y^2}^* \leftarrow d_{xy}$ spin-allowed transition. Therefore, this assignment, ${}^3A_1 \leftarrow {}^1A_1$ ($d_{x^2-y^2}^* \leftarrow d_{xy}$), was tentatively made for the band at 28,700 cm^{-1} in the a-z polarization. The more intense peak at 33,000 cm^{-1} in this polarization was assigned to the spin-allowed excitation, ${}^1B_1 \leftarrow {}^1A_1$ ($d_{x^2-y^2}^* \leftarrow d_{yz}$).

The large peak in the c-x polarization is clearly asymmetric, especially at room temperature. A peak maximum was resolved at 32,100 cm^{-1} . This band was assigned as the ${}^1A_2 \leftarrow {}^1A_1$ ($d_{x^2-y^2}^* \leftarrow d_{xz}$) transition. Theoretically, this transition should have zero ligand field transition moment and be vibronically excited in both the x and z polarization. This was verified experimentally, in that, the intensity decreased at lower temperatures. It should be noted that the ${}^1B_1 \leftarrow {}^1A_1$ transition in the a-z polarization is completely forbidden in the x polarization. The 1B_1 and 1A_2 excited states arise from the degenerate 1E_g state in D_{4h} symmetry.

The spectral assignments of dichloro(ethylenediamine)platinum(II), Pt(en)Cl_2 , can be directly related to Pt(en)Br_2 , the subject of this thesis. The solid state spectra of both these complexes exhibited unusual crystal effects. An oriented gas model could not be applied.

The planar molecules of Pt(en)Cl_2 stack as shown in Figure 7. The molecular axes chosen for this complex, Figure 7, are different than in the previous two cases. The local symmetry, C_{2v} , probably establishes the selection rules. When the puckering of the chelate ring is considered, the molecular symmetry is C_2 . For convenience, the C_2 symmetry axis is directed along the y molecular axis and the z axis is then perpendicular to the molecular plane, Figure 7. This means that the lowest unfilled, antibonding sigma orbital is the d_{xy} (b_2) in contrast to the two previous cases. The d-orbital ordering for D_{4h} and C_{2v} symmetries is shown in Figure 8.

The assignment of the solution spectrum bands follows that of Chatt et al. (1) and of the previously discussed complexes when the appropriate changes due to axes choice are considered. In Figure 9, the aqueous solution spectrum of Pt(en)Cl_2 as reported by Martin et al. (24) is shown. The assignments for the absorption bands are given in Table 2. Table 2 also contains the predicted ligand field polarizations in the crystal.

Jacobson and Benson (25) determined from X-ray diffraction data that the Pt(en)Cl_2 crystals belong to the orthorhombic system. The unit cell contains 4 molecules. The Pt(en)Cl_2 molecules stack in chains as shown in Figure 7. The Pt-Pt distance in the chains is fairly small,

Figure 7. Stacking of the $\text{Pt}(\text{en})\text{Cl}_2$ molecules. The orientation of the molecular and crystallographic axes

Figure 8. Orbital ordering under D_{4h} and C_{2v} for the axes selected for $Pt(en)Cl_2$

Figure 9. Aqueous solution spectrum and b polarized single crystal spectrum of $\text{Pt}(\text{en})\text{Cl}_2$ at 300°K

Table 2. Transitions in $\text{Pt}(\text{en})\text{Cl}_2$ from solution spectrum

Wave number cm^{-1}	Molar absorptivity $\text{M}^{-1} \text{cm}^{-1}$	Oscillator strength	Transition assignment C_{2v} symmetry $\leftarrow A_1$	Predicted ligand field polarization in crystal
24,900	12	1.7×10^{-4}	${}^3B_2(d_{xy}-d_{x^2-y^2})$	
27,300	31	5.1×10^{-4}	${}^3A_2(d_{xy}-d_{yz})$ ${}^3B_1(d_{xy}-d_{xz})$	
33,200	226	4.1×10^{-3}	${}^1B_2(d_{xy}-d_{x^2-y^2})$	$\underline{x} - \underline{a}$
36,900	94	1.6×10^{-3}	${}^1A_2(d_{xy}-d_{yz})$ ${}^1B_1(d_{xy}-d_{xz})$	Forbidden $\underline{z} - \underline{c}$
Not observed			${}^1B_2(d_{xy}-d_{z^2})$	$\underline{x} - \underline{a}$
49,200	6700	2.0×10^{-1}	${}^1B_1(d_{xy}-L\pi-a_2)$ ${}^1A_1(d_{xy}-L\pi-b_2)$ ${}^1B_2(d_{xy}-L\pi-a_1)$ ${}^1A_2(d_{xy}-L\pi-b_1)$	$\underline{z} - \underline{c}$ $\underline{y} - \underline{b}$ $\underline{x} - \underline{c}$ Forbidden

3.39 Å, whereas the Pt-Pt distance within the plane ranges from 7.5 to 8.1 Å. The crystals grow as thin platelets with 100 faces. Light incident perpendicular to this face is collinear with the x axis. Therefore, polarized light can be directed parallel to the c axis (z molecular axis) or parallel to the b axis (y molecular axis).

The crystal spectra of Pt(en)Cl_2 including both b and c polarizations at 300°K and 77°K are shown in Figure 10. These spectra and the following assignments were reported by Martin and coworkers (24). The b polarized crystal spectrum is shown in comparison to the solution spectrum in Figure 9. A weak absorption appears in the region of the spin-forbidden d-d bands perhaps slightly shifted to lower energy from the solution bands. The region of the spin-allowed d-d bands is dominated by an intense peak at $33,600 \text{ cm}^{-1}$ and a weaker band at $39,100 \text{ cm}^{-1}$. The $39,100 \text{ cm}^{-1}$ band is very close to the minimum in the solution spectrum. At liquid nitrogen temperature, 77°K, the $33,600 \text{ cm}^{-1}$ band in the b polarization has shifted to $33,100 \text{ cm}^{-1}$, narrowed in width and increased in peak height from $600 \text{ cm}^{-1} \text{ M}^{-1}$ to $710 \text{ cm}^{-1} \text{ M}^{-1}$. The $39,100 \text{ cm}^{-1}$ band also exhibited a dramatic increase in intensity at the lower temperature. There appears to be other unresolved absorption in the $32,000\text{--}36,000 \text{ cm}^{-1}$ region. This temperature dependence is in contrast with the K_2PtCl_4 spectra which consisted of vibronic transitions. This would indicate some dipole allowed character in these bands. It is seen in Table 2 that none of the spin-allowed d-d bands can have a ligand field dipole moment in the y or b polarization. As a result, these bands were assigned as ionized exciton

Figure 10. Polarized single crystal absorption spectra at 300°K and 77°K of Pt(en)Cl_2 . Diffuse reflectance spectrum of Pt(en)Cl_2 at 300°K

transitions by Martin et al. (24). These assignments will be discussed shortly in terms of ionic exciton states.

Considering the c polarization, the intensity in the spin-forbidden d-d region appears to be about 15 times greater than in the b polarization. The absorption peak also appears to have red shifted 3000 cm^{-1} from the $22,000\text{ cm}^{-1}$ value for the solution spectrum. The absorption in the c polarized spectrum becomes too high to measure beyond $31,000\text{ cm}^{-1}$ using single crystals. However, an absorption peak can be seen in the diffuse reflectance spectrum, Figure 10, which can be attributed to this intense peak in the c polarization. In the diffuse reflectance spectrum, the peak at $25,000\text{ cm}^{-1}$ corresponds to the spin-forbidden d-d transitions. It appears to follow the c polarization quite well. There is a shoulder at $34,000\text{ cm}^{-1}$. This occurs in the region of the d-d spin-allowed bands and also in the region of the first well-defined peak in the b polarization. The maximum at $37,500\text{ cm}^{-1}$ evidently corresponds to the intense absorption peak in the c polarization. Therefore, it has been concluded (24) that this is an intense dipole-allowed transition (or transitions) which is forbidden in the b polarized crystal spectrum and which occurs near the minimum of $40,500\text{ cm}^{-1}$ in the solution spectrum. This dramatic red shift of $12,500\text{ cm}^{-1}$ has been explained with exciton theory.

A. Frenkel Exciton States

In a crystal such as Pt(en)Cl_2 with two molecules per primitive cell, it is possible to have Davydov splitting of each excited molecular state into two crystal states. However, in this case one transition

has zero intensity due to the parallel alignment of the molecular axes and the uniform molecular distances along the chains. Hence, only one spectral transition is seen. This is equivalent to a case in which each molecule along the chain is translationally equivalent. Therefore, such a simpler treatment has been employed.

In the first consideration, the crystal was viewed as an aggregate of noninteracting oriented molecules in a rigid lattice. Perturbations resulted from intermolecular interactions. This type of treatment has been employed by Craig and Walmsley (26), Davydov (27) and others (28,29). The product of the ground state free molecule wave functions is the total ground state wave function

$$\Phi^0 = \varphi_1^0 \varphi_2^0 \dots \varphi_n^0 \dots \varphi_m^0 \dots \quad (1)$$

When molecule m absorbs light and the excited state is described by φ_m^1 , the localized excitation wave function becomes

$$\Phi_m^1 = \varphi_1^0 \varphi_2^0 \dots \varphi_n^0 \dots \varphi_m^1 \dots \quad (2)$$

If the crystal is large enough for cyclical boundary conditions, a suitable crystal wave function can be written from a complete set of localized excitation functions. This crystal wave function is

$$\Phi_k^1 = N^{-\frac{1}{2}} \sum \exp(i\mathbf{k} \cdot \mathbf{R}_m) \varphi_m^1 \quad (3)$$

These wave functions which comprise a band of energy states are the wave functions for Frenkel type excitons. However, in this model the only allowed absorptions are to the state with $\mathbf{k} = 0$, where $\mathbf{k}$ is the wave vector,

$$\Phi_0^1 = N^{-\frac{1}{2}} \sum \varphi_m^1 \quad (4)$$

The transition energy from the ground state to this excited state is

$$\bar{\nu}(\Phi_0^1 - \Phi^0) = \bar{\nu}_0 + D + I \quad (5)$$

where

$$D = \sum_n' \left[\int (\varphi_m^1 \varphi_n^0)^* |V_{m,n}| (\varphi_m^1 \varphi_n^0) d\tau - \int (\varphi_m^0 \varphi_n^0)^* |V_{m,n}| (\varphi_m^0 \varphi_n^0) d\tau \right] \quad (6)$$

and

$$I = \sum_n' I_{n,m} = \sum_n' \int (\varphi_m^1 \varphi_n^0)^* |V_{m,n}| (\varphi_m^0 \varphi_n^1) d\tau \quad (7)$$

The perturbation operator, $V_{m,n}$, represents the sum of all interactions between molecules m and n in the crystal. The transition energy for the molecule in the gaseous state is represented by $\bar{\nu}_0$. The $n = m$ terms are excluded on the summation with the prime.

In Equation 6, D describes the difference in van der Waal's energy between the ground and the excited state. This quantity is usually negative resulting in a lowering of the transition energy. In Equation 7, I is of the form of the Davydov splitting terms in crystal spectra. For dipole allowed transitions, an estimate of $I_{n,m}$ can be obtained with Equation 8,

$$I_{n,m} = e^2 R^{-3} (x_n^1 x_m^1 + y_n^1 y_m^1 - 2z_n^1 z_m^1) \quad (8)$$

where x_n^1 is the x component of the transition moment r^1 on atom n and likewise for the remaining components. Considering Equation 8, for Pt(en)Cl_2 a z polarized transition will be shifted to lower energy. For x or y polarizations, this shift is to higher energy. For a $1.0 \text{ \AA}^0$ z transition moment centered on the platinum atom, this shift was found to be about $-12,000 \text{ cm}^{-1}$. However, this is not totally accurate since a $\text{Pt} \leftarrow \text{Cl}$ charge transfer moment should not be centered on the platinum atom. When this transition moment was centered midway between the platinum atom and the center of mass of the two chlorine ligands, the

value of I was found to be only $-6,000\text{ cm}^{-1}$. As a result, it was proposed (24) that the intense z polarized absorption peak at $37,500\text{ cm}^{-1}$ was probably a charge transfer transition shifted from the $46,000$ - $53,000\text{ cm}^{-1}$ region in the solution spectrum. The I term of $-6,000\text{ cm}^{-1}$ does not account for the total shift. Therefore, the D term as well as solvent effects in the solution spectrum must make some contribution to the shift.

Similar shifts have been observed in other solid state spectra. For example, Craig and Hobbins (30) observed a Davydov shift of $16,000\text{ cm}^{-1}$ in the crystal spectrum of anthracene.

Considering Equation 8 with respect to x and y polarized transitions, the exciton theory requires these strongly allowed transitions to appear at much higher energies than the z polarized transition of similar energy in the free molecule. This allows the weak bands in the b polarization to be clearly visible. Martin and coworkers (24) observed that the maximum molar absorbances of these bands at $33,100\text{ cm}^{-1}$ and $39,100\text{ cm}^{-1}$ increased upon cooling to 77°K . This indicated that the bands were not exclusively vibronic excitations, but contained some dipole moment excitation. The band at $33,100\text{ cm}^{-1}$ coincided with a solution maximum, Figure 9. However, Martin and coworkers showed that these transitions would not have a nonzero transition moment in the b direction. Therefore, another explanation had to be found.

B. Ionized Exciton States

Frenkel excitons could not account for the two bands at $33,100\text{ cm}^{-1}$ and $39,100\text{ cm}^{-1}$ in the b polarization. Molecular and crystal symmetry

did not allow any perturbation contribution to a transition dipole in that direction. It was then postulated that these transitions involved the transfer of an electron from one molecule to an adjacent molecule, an ionic excitation. This type of excitation requires a significant amount of orbital overlap between neighboring molecules. Hence, only molecular interactions along the chain needed to be considered and any interaction between chains could be disregarded. This allows the problem to be treated as a one dimensional chain with the platinum d-orbitals overlapping. Only spin allowed transitions from a filled molecular orbital, u^0 , to a single unfilled orbital, u^1 , will be considered. Therefore, a ground state wave function can be written in a determinantal or antisymmetrized form

$$\Phi^0 = (N!)^{-\frac{1}{2}} |\dots u_{j-2}^0 u_{j-1}^0 u_j^0 u_{j+1}^0 u_{j+2}^0 \dots| \quad (9)$$

The index, j , identifies the molecule and runs from $-(N-1)/2$ to $+(N-1)/2$ for the N molecules in the chain. The excited state wave function for an electron being excited from an orbital u_j^0 to an excited orbital $u_{j+\beta}^1$ is of the form

$$\Phi_j^1(\beta) = (N!)^{-\frac{1}{2}} |\dots u_{j-2}^0 u_{j-1}^0 u_j^0 \dots u_{j+\beta}^1 \dots| \quad (10)$$

This electron transfer results in leaving molecule j with a positive charge and molecule $j+\beta$ with a negative charge. An excitation of this type is shown schematically for $\beta = +1$ in Figure 11. The transition illustrated is from u^0 , the d_{z^2} orbital, to u^1 , the d_{xy}^* orbital. The complete exciton problem for a one dimensional crystal has been treated by Merrifield (31). Merrifield first treated the Frenkel or molecular excitation. He then considered a series of bands based on bound

Figure 11. Schematic of an ionic excitation, $(d_{xy}^*)_{j+1} \leftarrow (d_{z^2})_j$

ionic states, in which, the electron and hole are bound together by the coulombic attraction but can migrate as a pair through the crystal.

Finally, Merrifield considered a series of conduction bands at higher energies. In these bands the electron and hole can move independently.

In the case of ionized exciton states, the crystal wave functions are of the form

$$\Phi'_0(\beta) = N^{-\frac{1}{2}} \sum_j \phi_j(\beta) \quad (11)$$

where k values are zero and $\beta \neq 0$ as compared to the Frenkel excitons where both the k values and β were zero. The crystal wave functions are degenerate for $\beta = \pm 1$. Therefore, the following linear combinations are possible

$$\Psi'_+(\beta) = 2^{-\frac{1}{2}} [\Phi'_0(\beta) + \Phi'_0(-\beta)] \quad (12)$$

and

$$\Psi'_-(\beta) = 2^{-\frac{1}{2}} [\Phi'_0(\beta) - \Phi'_0(-\beta)] \quad (13)$$

Since the set $\Psi'_+(\beta)$ has the same symmetry properties as the Frenkel state $\Phi'_0(0)$, it interacts with it. Since a transition to a Frenkel state is forbidden in the $\underline{b}$ polarization, the transitions to $\Psi'_+(\beta)$ states are also forbidden. According to Martin and coworkers (24) the transition moment for an ionic exciton transition to the $\Psi'_-(1)$ state is

$$\begin{aligned} \int \Phi^{0*} | \sum r_i | \Psi'_-(1) d\tau &= (2N)^{-\frac{1}{2}} \left[\sum_j \int u_j^{0*} | r | u_{j+1}^1 d\tau - \sum_j \int u_j^0 | r | u_{j-1}^1 d\tau \right] \\ &= (N/2)^{\frac{1}{2}} [r_{j,j+1}^1 - r_{j,j-1}^1] \end{aligned} \quad (14)$$

where $\beta = 1$. The term $r_{j,j+1}^1$ corresponds to the transition moment for an electron transfer from u_j^0 to u_{j+1}^1 . When the total transition dipole moment is nonzero, the transition is allowed. The transition dipole

moment is nonzero when

$$r_{j,j-1}^1 = -r_{j,j+1}^1 \neq 0 \quad (15)$$

Because of the alignment of the Pt(en)Cl_2 molecules along the stacking axis, Martin and coworkers were able to formulate selection rules for possible transitions. The symmetry properties of the orbitals involved are shown in Figure 12. This figure will assist in applying the selection rules. The square in each sketch represents a section halfway between Pt atoms in two adjacent molecules, j and $j+1$, in the chain. In each section, the solid line is an outline of the ground state orbital, u_j^0 , and the dashed line, an outline of the excited orbital, u_{j+1}^1 . Since the d_{xy}^* orbital is unfilled, it will always be the excited orbital, u_{j+1}^1 . In each sector the signs of the $\underline{x}$, $\underline{y}$ and $\underline{z}$ components of the product $u_j^0 r^1 u_{j+1}^1$ appear in parentheses, respectively. The origin is considered to be on the Pt atom of the j th molecule. A transition is dipole forbidden when the positive values of the $\underline{x}$, $\underline{y}$ or $\underline{z}$ components in some sectors are exactly cancelled by the respective negative values in other sectors. As shown in Figure 12, this is the case for $(d_{xy}^*)_{j+1} \leftarrow (d_{z^2})_j$ and $(d_{xy}^*)_{j+1} \leftarrow (d_{x^2-y^2})_j$. For the transition $(d_{xy}^*)_{j+1} \leftarrow (d_{xz})_j$, the $(\underline{y}')_{j,j+1}$ component is found to be positive in each sector. Hence, it is a dipole allowed transition in the $\underline{y}$ or $\underline{b}$ polarization. Martin and coworkers assigned the band at $33,100 \text{ cm}^{-1}$ to this transition. It is evident from symmetry that the transition $(d_{xy}^*)_{j+1} \leftarrow (d_{yz})_j$ will have a nonzero transition moment in the $\underline{x}$ direction.

The second dipole allowed band in $\underline{b}$ polarization will now be

Figure 12. Symmetry properties of the ionic excitation transfer moments $\underline{r}_{j,j+1}^i$ for transitions from orbitals on the j th molecule to $(d_{xy}^*)_{j+1}$

considered, also in terms of exciton theory. Martin and coworkers (24) proposed for this band at $39,100\text{ cm}^{-1}$ an excitation to an ionic exciton state which resulted from a charge transfer transition, $d_{xy}^* \leftarrow L(\pi)$. The symmetry of the chloride σ and π orbitals allows only one transition to have nonzero values for $y'_{j,j+1} = y'_{j,j-1}$. This was found to be the a_2 nonbonding π orbital. The transition was assigned as $(d_{xy}^*)_{j\pm 1} \leftarrow (L(\pi) - a_2)_j$. The symmetry properties for this transition appear in Figure 12E. A summary of the band assignments for the crystal spectra of Pt(en)Cl_2 appears in Table 3.

This was the first evidence for ionic exciton states in complexes involving a transition metal. In order to learn more about this phenomena, more complexes which exhibit these unusual excited states needed to be found. The first complex to be considered was the bromide analogue of Pt(en)Cl_2 . It is the subject of this thesis. Another complex which was considered to be a good candidate was Magnus' green salt, $\text{Pt}(\text{NH}_3)_4\text{PtCl}_4$. Crystals of Magnus' green salt, MGS, have a deep green color. The Pt-Pt distance in MGS is only $3.24\text{ \AA}$, which is shorter than in Pt(en)Cl_2 . However, using low temperature spectra Martin and coworkers (32) recently showed that MGS does not have any spectroscopically accessible ionic excitations. In MGS, this excitation would involve an electron transfer between charged species. Evidently, this causes the transition to be at too high energy to be observed.

Table 3. Crystal spectra of Pt(en)Cl_2

Wave number cm^{-1}	Polarization	Oscillator strength, at 77°K	Proposed assignment: excitation
19,000-27,000	<u>c</u>	9×10^{-3}	$d \leftarrow d$, spin forbidden: vibronic and ligand field
22,000-27,000	<u>b</u>	4×10^{-4}	$d \leftarrow d$, spin forbidden: vibronic and ligand field
28,000	<u>b</u>	$\sim 5 \times 10^{-4}$	$d_{xy} \leftarrow d_{x^2-y^2}$, spin allowed: vibronic
33,100	<u>b</u>	1.7×10^{-3}	$d_{xy} \leftarrow d_{xz}$: ionized exciton $\beta_{xy} = \pm 1$. Dipole allowed by overlap
37,500	<u>c</u>	($\sim 0.2?$)	$d_{xy} \leftarrow L\pi - a_2(6p_z \leftarrow 5d_{z^2})$: Frenkel exciton, dipole allowed
39,100	<u>b</u>	1.3×10^{-3}	$d_{xy} \leftarrow L\pi - a_2$: ionized exciton $\beta_{xy} = \pm 1$. Dipole allowed by overlap

11. EXPERIMENTAL

The Pt(en)Br_2 was prepared according to the method of Watt and McCarley (33). A solution of potassium tetrabromoplatinate(II) was treated at room temperature with 0.1 ml portions of 1:10 aqueous ethylenediamine. Yellow crystals of Pt(en)Br_2 precipitated from solution. The product was purified by dissolving in N,N-dimethylformamide, from which it recrystallized upon addition of water.

Very thin, flat crystals of the compound were grown by evaporating a water solution containing about 0.01 M KBr and saturated with Pt(en)Br_2 . The crystals were removed from the solution and fastened over a pinhole in a platinum plate with low temperature varnish. The pinholes were typically 0.6-0.8 mm in diameter, whereas, the crystals had an area of 1-2 mm². The platinum plate was then mounted in the copper cold finger of a liquid helium cryostat. The cold finger was insulated by a vacuum and a bright copper radiation shield. Two quartz windows in the tail section provided a pathway for the light beam. The tail section of the cryostat was then placed in the sample beam of a Cary 14 spectrophotometer. A pinhole and, if necessary, neutral density screens were placed in the reference beam. A Glan-type calcite polarizer was placed in the sample light beam after the crystal. An identical polarizer was placed in the same position in the reference beam. This balanced out any polarizer effects caused by either calcite absorption bands or systematic polarization within the spectrophotometer. A high intensity light source Model 1471200 was used from 600 nm to about 280 nm.

The hydrogen arc was used for the uv spectrum, 280 nm to 190 nm. Spectra were recorded at room temperature, 77°K and 15°K for the c polarization and b polarization. The cryogenic spectra were obtained by adding liquid nitrogen, 77°K, to the cryostat which was then replaced with liquid helium to provide 15°K, nominally. In all spectra the absorbance at 600 nm was set equal to zero, since there was no evident absorption at that wavelength. Baselines for both polarizations were determined at room temperature under the same conditions as the crystal spectra. In most cases a pinhole similar in size to the pinhole with the crystal was used for the baseline determination. Both spectra and baselines were automatically recorded on computer cards by a Cary-Datex digitalization system. The I PLOT program written by L. D. Hunter (34) subtracted the baselines and plotted the spectra.

The molar absorbance of the crystals was based on the well-known relationship

$$\epsilon = OD/Lc \quad (\text{cm}^{-1} \text{M}^{-1}) \quad (16)$$

(OD = optical density or absorbance, L = path length or crystal thickness, c = concentration). The absorbance, OD, was measured at 410 nm in the c polarization of the crystal spectra. The Lc term was determined using three different methods. A method utilized in previous work (18,24,34) is based on an indirect determination of the crystal thickness from the crystal's weight and surface area. The following known terms are substituted into Equation 16:

$$c = (\text{wt}/\text{MW})/V \quad (17)$$

$$L = V/A \quad (18)$$

(wt = weight of the crystal (g), MW = molecular weight (g/mole),

V = volume and A = surface area (cm²)). Thus,

$$\begin{aligned}\epsilon &= OD / ((V/A) \times (wt/MW)/V) \\ &= (OD \times MW \times A \times 10^{-3}) / wt \quad \text{cm}^{-1} \underline{M}^{-1} \quad (19)\end{aligned}$$

For this molar absorbance determination, relatively large, uniformly thick crystals were needed. Large crystals of Pt(en)Br₂ which had both uniform thickness and uniform extinction could not be grown. The crystal which was used had an area of 0.404 mm² and a weight of 1.81 x 10⁻⁵ g. A Cahn microelectrobalance was used to determine the weight of the crystal. The molar absorbance for this crystal was found to be 299 cm⁻¹ M⁻¹ at 410 nm in the c polarization. This result was estimated to have an uncertainty of as much as 10%.

The thickness of another crystal was estimated using a calibrated eyepiece in the polarizing microscope. Its thickness was estimated to be 5(±1) x 10⁻⁴ cm. From the thickness and the density, 3.704 g/cm³ (34), the molar absorbance was determined using Equation 16. The molar absorbance at 410 nm in the c polarization was found to be 272 cm⁻¹ M⁻¹ with an uncertainty of 20%.

The third method used to determine the molar absorbance of Pt(en)Br₂ was based on the analysis of interference effects. Periodic variations in the absorbance with wave length were recorded in regions of low absorbance for crystals having surfaces of sufficient optical quality (32). Such periodic fluctuation, shown in Figure 17, was observed for two Pt(en)Br₂ crystals. This fluctuation was evidently due to the constructive and destructive interference of light which

reflected off of the crystal faces, Figure 13. This phenomena was observed for crystals which were very thin, $10\ \mu$ or less for Pt(en)Br_2 , were uniformly thick, exhibited one interference color between the crossed polarizers and had good optical surfaces.

The change in phase of light, δ_o , which has reflected from two crystal surfaces which are normal to the light beam, is given by the expression (35),

$$\delta_o = 4\pi L n / \lambda^o \quad (20)$$

(λ^o = wave length in vacuum, n = refractive index, and L = crystal thickness). The minimum absorbances represent points of maximum transmission, that is, the reflected light interferes constructively making $\delta_o/2\pi$ an integer. Similarly, absorbance maxima, transmission minima, represent destructive interference by the reflected light beam. If $\delta_o/2\pi$ is the integer N , then the adjacent absorption minimum is $N-1$ provided $\lambda_{N-1} > \lambda_N$. From Equation 20

$$N\lambda_N/n_N = (N-1)\lambda_{N-1}/n_{N-1} \quad (21)$$

Over small wave length regions, $\sim 10\ \text{nm}$, the refractive index should not change significantly and n_N and n_{N-1} should cancel in Equation 21. The value of N can then be determined from the two wave length readings alone. The crystal for this experiment was unusually thin having only four observed minima at 544.4, 441.9, 375.4 and 330.4 nm with the crystal normal to the beam. The value of N found for the first minimum, 330.4 nm, was 8.3. The relatively large deviation of this value from the integral value was due to the large distance between adjacent minima resulting in a significant change in the index of refraction. This

Figure 13. Light path through a thin crystal section

approximate value of N was checked by calculating a ratio, from Equation 21, of n at each maximum and minimum to n at a chosen maximum or minimum. More specifically, if $n_{375.4}$ was the index of refraction at 375.4 nm, the ratio of $n_{\lambda}/n_{375.4}$ was calculated for each of the maxima and minima. This ratio was then plotted versus wave length or wave numbers by means of a quadratic least squares computer program. The resulting plot showed the wave length dependence of the refractive index. Several of these plots were made for different sets of N values. For example, when $N = 7$ at 375.4 nm the plot had a maximum. The index of refraction was expected to generally increase with decreasing wave length making this first set of N values unacceptable. Another plot was made in which $N = 6$ at 375.4 nm. This plot contained no maximum and had an acceptable slope, $\sim 6\%$. A third plot in which $N = 5$ at 375.4 nm yielded a larger slope which gave a 21% change in n_b between 330.4 nm and 544.4 nm. Such a large change in the refractive index with wave length is not expected. Therefore, the values of $N = 4, 5, 6$ and 7 were assigned to the respective minima, 544.4, 441.9, 375.4 and 330.4 nm.

An approximate value for the refractive index about the b axis can be determined by observing the shift in the absorbance minima when the crystal is rotated by an angle, θ_i , about its c axis. The tilt of the crystal on the pinhole was determined and corrected for by using both positive and negative rotations. In the following derivation and eventual calculation of the index of refraction, an assumption was first made that n_a , the refractive index along the a axis, is equal

to n_b , the refractive index along the $\underline{b}$ axis. This is equivalent to making the crystal uniaxial with $\underline{c}$ the optic axis. For an orthorhombic crystal like Pt(en)Br_2 , this is not true. However, it will be shown that in this case, in which the angle of refraction is small the actual value of n_b is likely within the uncertainty of the experimental value of the refractive index. This assumption also implies that Snell's law, Equation 25, can be applied. This law is not valid when n_a is not equal to n_b .

Since the angle of incidence, θ_i , is known, it is necessary to find the angle of refraction, θ_r , of the wave front. The angle of refraction can be approximated from the ratio of the phase delays, $\delta_{\theta_i}/\delta_o$, where δ_{θ_i} is the phase delay of the wave front for the angle of rotation or incidence, θ_i . The phase delay for the crystal normal to the beam, δ_o , is given by Equation 20 where n is specifically the refractive index in the $\underline{b}$ direction at a given wave length, λ . The phase delay at θ_i is

$$\delta_{\theta_i} = (4\pi L n_{\theta_i, \lambda}) / (\cos \theta_r \lambda^0) - (4\pi L \tan \theta_r \sin \theta_i) / \lambda^0 \quad (22)$$

where the first term represents the phase delay caused by the reflection of the beam on the inner crystal surfaces, upper beam in Figure 13, and the second term results from the additional distance the lower beam must travel in order to reach the crystal and interfere with the reflected beam. When Equation 22 is divided by Equation 20, the phase delay for the crystal normal to the light beam, Equation 23 is obtained.

$$\delta_{\theta_i, \lambda} / \delta_{o, \lambda} = ((n_{\theta_i, \lambda} / \cos \theta_r) - \tan \theta_r \sin \theta_i) / n_{b, \lambda} \quad (23)$$

By factoring, Equation 24 results

$$\delta_{\theta_i, \lambda} / \delta_{o, \lambda} = ((1/\cos \theta_r) - (\tan \theta_r \sin \theta_i / n_{\theta_i, \lambda})) (n_{\theta_i, \lambda} / n_{b, \lambda}) \quad (24)$$

Assuming Snell's law, Equation 25, is valid

$$n = \sin \theta_i / \sin \theta_r \quad (25)$$

a substitution for $n_{\theta_i, \lambda}$ is made yielding Equation 26.

$$\delta_{\theta_i, \lambda} / \delta_{o, \lambda} = (n_{\theta_i, \lambda} / n_{b, \lambda}) \cos \theta_r \quad (26)$$

This is an expression of the ratio of the phase delay for the tilted crystal to the phase delay for the crystal normal to the light beam at a given wave length assuming $n_a = n_b$. Now, solving for $\cos \theta_r$,

$$\cos \theta_r = (\delta_{\theta_i, \lambda} / \delta_{o, \lambda}) (n_{b, \lambda} / n_{\theta_i, \lambda}) \quad (27)$$

Now

$$\delta_{\theta_i, \lambda} / \delta_{o, \lambda} = \delta_{o, \lambda'} / \delta_{o, \lambda} \quad (28)$$

where λ' is the wavelength of the minimum which has the same value of N as the minimum corresponding to N at λ for θ_i degrees tilt.

Substituting Equation 20,

$$\delta_{\theta_i, \lambda} / \delta_{o, \lambda} = (n_{b, \lambda'} / n_{b, \lambda}) \quad (29)$$

Now

$$\cos \theta_r = (n_{b, \lambda} / n_{\theta_i, \lambda}) (n_{b, \lambda'} / n_{b, \lambda}) (\lambda / \lambda') \quad (30)$$

The ratio of $n_{b, \lambda'}$ to $n_{b, \lambda}$ can be approximated as one for values of $\lambda' - \lambda$ less than 10 nm. However, this approximation could not be used for the Pt(en)Br_2 crystal which was studied. This ratio was obtained from the quadratic least squares plot of the dependence of the refractive index on wave length. The second ratio of refractive indices in Equation 30, $n_{b, \lambda} / n_{\theta_i, \lambda}$, is equal to one for tetragonal crystals such as Magnus' Green salt (32). However, Pt(en)Br_2 has an orthorhombic

structure and this ratio is not equal to one. It would be expected that for relatively small values of θ_r this ratio would be very close to one. Therefore, in the calculation of the refractive index this ratio was assumed to be one. Then, using Snell's law, Equation 25, which in this case is only an approximation, an average index of refraction was determined for a given angle of rotation, θ_i . The experimental value, n , is not exactly the index of refraction at the angle θ_i , nor is it exactly n_b . However, since the angle of refraction is small, 18.4° , these three values are very similar. A value of 1.85 ± 0.10 was determined for the index of refraction at $\theta_i = \pm 30^\circ$.

The following test was undertaken to determine the error which would result from a value of n_a as low as 1.56. In determining the angle of refraction, θ_r , a Huygenian construction, Figure 14, must be employed (36). This construction takes into account the inequality of n_a and n_b with the ellipse shown in Figure 14. The distance from the origin to the side of the ellipse in the y direction is $1/n_b$ and in the x direction, $1/n_a$. The wave front in the crystal is tangent to the ellipse. At the point of tangency, the refracted light ray intersects the ellipse. The direction of the wave front, shown by the line through the origin and normal to the wave front, is not the same as the direction of the ray. Therefore, the angle of refraction for the wave front is different than the angle of refraction of the ray. It is this angle of refraction for the wave front which must be considered in terms of the observed interference waves. Wahlstrom (36) employs the equation for a tangent to an ellipse, Equation 31, in determining the angles of refrac-

Figure 14. Huygenian construction for a uniaxial crystal with an angle of incidence of 30° where WF = wave front

tion for the light ray and the wave front.

$$(x_1 x)/(1/n_a^2) + (y_1 y)/(1/n_b^2) = 1 \quad (31)$$

The value of n_b was approximated by using the experimental value of 1.85. The value of 2.0 for y , where y is the distance from 0 to $0'$, was determined from the triangle $OA0'$. Letting $x = 0$, Equation 32,

$$y_1 y n_b^2 = 1 \quad (32)$$

yielded a value of 0.146 for y_1 . Now, using an equation for the ellipse,

$$(x_1)^2/(1/n_a^2) + (y_1)^2/(1/n_b^2) = 1 \quad (33)$$

The value of x_1 was found to be 0.618. Since the slope of the refracted ray is now known from y_1 and x_1 , the angle of refraction for the ray can be determined from Equation 34.

$$\tan \theta_{r,ray} = y_1/x_1 \quad (34)$$

It was found to be 13.3° . Likewise, the angle of refraction for the wave front was determined from the slope of the normal to the tangent line which is given in Equation 35

$$-dx/dy = \tan \theta_{r,WF} = y_1 n_b^2 / x_1 n_a^2 \quad (35)$$

This yielded a value of 18.4° for the angle of refraction for the wave front.

The refractive index of this crystal was determined with polarized light incident between two crystal axes, a and b, and parallel to the third, c. This refractive index, n , is a combination of the refractive indices about the a and b axes, n_a and n_b . According to Wahlstrom (36), the relationship of n , n_a and n_b can be expressed in terms of an ellipse,

as shown in Equation 36,

$$(n \sin \theta_r)^2/n_a^2 + (n \cos \theta_r)^2/n_b^2 = 1 \quad (36)$$

Solving for n_b^2 ,

$$n_b^2 = (n_a n \cos \theta_r)^2 / (n_a^2 - n^2 \sin^2 \theta_r) \quad (37)$$

where $n_a = 1.56$, assumed minimum value

$n = 1.85$, experimental value

$\theta_r = 18.4^\circ$, angle of refraction for the wave front

Using Equation 37 a value of 1.89 was found for n_b , which is within the experimental error of ± 0.10 for n . Therefore, n_b is essentially equal to n , 1.85 ± 0.10 . Upon the application of this result to the spectrum which appears in Figure 17, Crystal #7, a value of $L = 1.6 \times 10^{-4}$ cm was found for the thickness which yielded a molar absorbance of $261 \text{ cm}^{-1} \underline{M}^{-1}$ at 410 nm. The error in the molar absorbance was estimated to be 10%.

Considering the three values for the molar absorbance and their respective uncertainties, an overall value of $279 \text{ cm}^{-1} \underline{M}^{-1}$ with an uncertainty of less than 7% was determined. This value applies to the c polarized spectrum at 410 nm ($24,390 \text{ cm}^{-1}$) at 300°K . The remaining molar absorbances in both polarizations were determined as a ratio to this value.

III. RESULTS AND DISCUSSION

The spectrum of Pt(en)Br_2 in aqueous solution is shown in Figure 15. Transition assignments for the solution spectrum have been summarized in Table 4. The absorption band positions, intensities, and approximate areas found in Table 4 and Table 5 were determined with the aid of a curve fitting computer program based on work by Siano and Metzler (37) and Fletcher and Powell (38). Basically, the assignments agree with proposals previously made by Chatt *et al.* (1), Martin *et al.* (24) and Martin (19). The low energy spectrum was recorded for an aqueous solution containing 0.318 M KBr, which suppressed aquation of the complex. The solution for the high energy spectrum did not contain any KBr because of Br^- ion interference. For this region the complex was rapidly dissolved in water and its spectrum recorded as quickly as possible.

This complex, Pt(en)Br_2 , had a crystal structure and molecular orientation very similar to Pt(en)Cl_2 . Hunter (34) found the space group for Pt(en)Br_2 to be orthorhombic, $C222_1$, with $a:b:c = 12.89:8.27:6.99 \text{ \AA}$. The crystallographic and molecular axes are shown in Figure 16. The planar Pt(en)Br_2 molecules stack in linear arrays with the Pt-Pt distance along the chain being $3.50 \text{ \AA}$. The Pt-Pt distance in Pt(en)Cl_2 was $3.39 \text{ \AA}$. Crystals which grew as thin plates were used for spectra determination. Generally, the Pt(en)Br_2 crystals were smaller, thinner and more fragile than those of Pt(en)Cl_2 . The edges of the plates were parallel to the $\underline{c}$ and $\underline{b}$ crystallographic axes. The $\underline{a}$ direction was perpendicular to the face of the plate. Therefore, the spectrophotometer

Figure 15. Aqueous solution spectrum and b polarized single crystal spectrum of Pt(en)Br_2 at 300°K

Table 4. Transitions in Pt(en)Br₂ from solution spectrum

Wave number cm ⁻¹	Molar absorptivity $\underline{M}^{-1} \text{ cm}^{-1}$	Oscillator strength	Transition assignment C _{2v} symmetry ← A ₁	Predicted ligand field polarization in crystal
26,700	47	1.2 × 10 ⁻³	³ B ₂ (d _{xy} ← d _{x²-y²}) ³ A ₂ (d _{xy} ← d _{yz}) ³ B ₁ (d _{xy} ← d _{xz})	-
31,400	283	4.7 × 10 ⁻³	¹ B ₂ (d _{xy} ← d _{x²-y²})	<u>x</u> - <u>a</u>
35,000	172	3.9 × 10 ⁻³	¹ A ₂ (d _{xy} ← d _{yz}) ¹ B ₁ (d _{xy} ← d _{xz})	Forbidden <u>z</u> - <u>c</u>
Not observed			¹ B ₂ (d _{xy} ← d _{z²})	<u>x</u> - <u>a</u>
44,000	(3000)	(3.6 × 10 ⁻²)	¹ B ₁ (d _{xy} ← Lπ-a ₂)	<u>z</u> - <u>c</u>
47,500	(7000)	(1.2 × 10 ⁻¹)	¹ B ₂ (d _{xy} ← Lπ-b ₂) ¹ B ₂ (d _{xy} ← Lπ-a ₁) ¹ A ₂ (d _{xy} ← Lπ-b ₁)	<u>y</u> - <u>b</u> <u>x</u> - <u>c</u> Forbidden

Figure 16. Stacking of the $\text{Pt}(\text{en})\text{Br}_2$ molecules. The orientation of the molecular and crystallographic axes

light beam could be polarized parallel to the $\underline{c}$ and the $\underline{b}$ direction for absorption measurements.

The single crystal polarized absorption spectra of Pt(en)Br_2 at 300°K and 15°K are shown in Figure 17. The $d \leftarrow d$ spin-forbidden bands appear at lower energy in the $\underline{b}$ polarized Pt(en)Br_2 spectra than in the spectra of Pt(en)Cl_2 , Figure 10. Similarly, in the $\underline{c}$ polarization the $d \leftarrow d$ spin-forbidden bands are at lower energy for Pt(en)Br_2 than for Pt(en)Cl_2 . These results are consistent with the position of bromide, less than chloride, in the spectrochemical series. The spin-allowed transition, $d_{xy}^* \leftarrow d_{x^2-y^2}$, in the $\underline{b}$ polarized spectra of Pt(en)Br_2 appears at $31,000 \text{ cm}^{-1}$. This is 3000 cm^{-1} higher than the energy of the corresponding transition in Pt(en)Cl_2 and therefore appears to be inconsistent with the spectrochemical series. However, when the uncertainty in the intensity and position, Figure 10, of the transition in Pt(en)Cl_2 is considered, it is evident that this value is very approximate. The spectrum of Pt(en)Br_2 having a much better defined peak, Figure 17, yields a more accurate value for the energy of this transition.

The ionized exciton, $d_{xy}^* \leftarrow d_{xz}$, appeared at $33,500 \text{ cm}^{-1}$ in the $\underline{b}$ polarized spectra of Pt(en)Br_2 . This was a shift of 400 cm^{-1} to higher energy from the corresponding transition in Pt(en)Cl_2 . In this case, the shift was a function of the position of bromide in the spectrochemical series and the intermolecular distance. Considering the spectrochemical series, the transition should have been shifted to lower energy. However, since the transition was intermolecular, its energy was also dependent on the intermolecular distance. The

Figure 17. Polarized single crystal absorption spectra at 300°K and 15°K of Pt(en)Br_2 . Diffuse reflectance spectrum of Pt(en)Br_2 at 300°K

intermolecular distance in Pt(en)Br_2 was $3.50 \text{ \AA}$, Figure 16, whereas it was only $3.39 \text{ \AA}$ in Pt(en)Cl_2 , Figure 7. A larger intermolecular distance caused a shift to higher energy. The net result was the observed shift of only 400 cm^{-1} .

The Frenkel exciton, $d_{xy}^* \leftarrow L\pi$, appeared at $36,700 \text{ cm}^{-1}$ in the c polarized spectra of Pt(en)Br_2 . The transition has been shifted 800 cm^{-1} to lower energy from the corresponding transition in Pt(en)Cl_2 . This red shift of the charge transfer bands was also observed in the b polarization. The very intense charge transfer bands in the b polarization have red shifted sufficiently that the second ionized exciton was not observed. In Pt(en)Cl_2 , this ionized exciton appeared at $39,100 \text{ cm}^{-1}$. The absorption of Pt(en)Br_2 at 300°K became too high to measure at $38,000 \text{ cm}^{-1}$. Likewise, the spectrum at 15°K did not show any conclusive evidence for a transition in this region. The assignments for Pt(en)Br_2 have been summarized in Table 5.

Table 5. Crystal spectra of Pt(en)Br₂

Wave number cm ⁻¹	Polarization	Oscillator strength: at 15°K	Proposed assignment: excitation
18,000-28,000	<u>c</u>	4.6×10^{-3}	d ← d, spin forbidden: vibronic and ligand field
18,000-28,000	<u>b</u>	1.8×10^{-3}	d ← d, spin forbidden: vibronic and ligand field
31,000	<u>b</u>	2.9×10^{-3}	d _{xy} ← d _{x²-y²} , spin allowed: vibronic
33,500	<u>b</u>	1.4×10^{-3}	d _{xy} ← d _{xz} : ionized exciton β = ±1. Dipole allowed by overlap
36,700	<u>c</u>	High	d _{xy} ← Lπ - a ₂ (6p _z ← 5d _{z²}): Frenkel exciton, dipole allowed

IV. SUMMARY

Polarized single crystal spectra have been recorded for Pt(en)Br_2 at 300°K and 15°K. The proposed assignments for the observed transitions have been tabulated in Table 5. These results have provided further evidence for the existence of unusual excited crystal states, ionized excitons, in transition metal coordination complexes.

Hunter (34) and Martin et al. (24) were the first to provide the temperature dependence of the absorption bands as evidence for these unusual excitations in coordination complexes. Now, it remains to study related systems in order to further test these assignment proposals. One related system may be the tetracyano-platinate(II) salts. Krogman (39) noted several of these complexes as having short Pt-Pt distances and anomalous colors. In addition to platinum systems, nickel and palladium complexes should also be considered. Future work in these areas will depend on the crystal structure of the complex, the physical shape of the crystal and the physical properties of the crystal.

V. BIBLIOGRAPHY

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