pressed earlier, that there are rather subtle criteria for stability of these complexes. The only stable complex (stable to loss of one ligand) is $[\{(C_6H_5)_3P\}_2Pt(CNCH_3)_2I][BF_4]$; we suspect that this has a trigonal-bipyramidal structure with phosphines in trans (axial) positions. Diphos, which chelates cis positions, could not give an analogous complex. Not so clear, however, is an explanation for the reaction of two nucleophilic groups with the diphos complex, leading to an uncharged complex. No disubstitution products were found in the reaction of the triphenylphosphine complexes except with organolithium compounds. In view of the relatively facile nature of these reactions, it is somewhat hard to picture this as a kinetic phenomenon, and one cannot make a strong case using trans-effect arguments. Presumably, for reactions of complexes of triethyl- and triphenylphosphine, several thermodynamic effects (including heat of solvation) control how many groups substitute.

Acknowledgments. We are pleased to acknowledge support from the National Science Foundation through Grants No. GP-8140 and GP-17207, and from the University of Wisconsin Graduate School.

Polarized Crystal Absorption Spectra for Dichloro(ethylenediamine)platinum(II). Evidence for Ionic Exciton States[1]

Don S. Martin, Jr.,* LeRoy D. Hunter, Roy Kroening, and Ronald F. Coley

Contribution from the Institute for Atomic Research and the Department of Chemistry, Iowa State University, Ames, Iowa 50010.

Received December 14, 1970

Abstract: In $Pt(en)Cl_2$ crystals, flat molecules stack in chains along an orthorhombic *c* axis. Crystal absorption spectra at 300 and 77 °K with light polarized in the *b* and *c* directions are reported for the region 18,000–42,000 cm^{-1}. These spectra indicate pronounced crystal effects from comparisons with the solution spectrum. A one-dimensional exciton theory is applied which accounts for the observed features. A dipole-allowed transition, $d_{xy} \leftarrow L(\pi)$, has been shifted from ~49,000 to 37,500 cm^{-1} with *c* polarization by crystal perturbations. In *b* polarization the temperature dependence indicates some allowed character to two weak bands at 33,100 and 39,100 cm^{-1}. These two bands have been assigned as unusual transitions to ionized exciton states based on the excitation of an electron into a d_{xy} (σ antibonding orbital) from the d_{xz} and $L(\pi)$ orbitals on adjacent molecules, respectively.

In a recent X-ray diffraction study, Jacobson and Benson[2] have shown that crystals of $Pt(en)Cl_2$ belong to the orthorhombic system, space group $C222_1$, $a:b:c = 12.44:8.12:6.78$ Å with four molecules per unit cell. The nearly planar molecules stack in a nearly linear array as shown in Figure 1 along the *c* axis. The crystal symmetry requires a uniform spacing between adjacent platinum atoms of 3.39 Å. These chains of stacked molecules are arranged in approximately a close-packed manner, so each molecule is surrounded by six neighbors in a plane with the Pt–Pt distances in the range of 7.5–8.1 Å. Each molecule in a 001 plane has the same orientation in space. The crystals have an exceptionally ideal orientation for spectral studies since the chains are directed along the orthorhombic *c* axis, and the symmetry axis and dipole moment of every molecule are in the $\pm b$ direction. It is possible to obtain directly, therefore, the absorption spectra with polarizations in these two important molecular directions.

A preliminary note concerning the crystal spectra was published earlier.[3] In that work the existence of an absorption peak with *b* polarization was noted which becomes narrower but higher at lower temperatures. Such behavior is not characteristic of vibronic excitation. A band theory in which the platinum d electrons were delocalized along the chains was proposed to account for this behavior. However, certain features of the crystal spectra did not appear consistent with such a delocalization. Consequently, exciton theory, which has proved so effective with aromatic organic molecular crystals,[4] has been applied to the interpretation of these spectra. The alignment of the molecules with respect to orthorhombic axes and the close approach of the platinum atoms provided some effects which are not usually encountered in the aromatic crystals. However, the fine structure which is commonly encountered with organic molecules does not occur with this coordination compound.

The present work includes crystal spectra of considerably higher quality than the earlier report, as thinner crystals have been obtained. It has been possible to extend the spectral range to shorter wavelengths and, in addition, certain limitations of the instrumenta-

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(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2822.

(2) R. A. Jacobson and J. E. Benson, private communication.

(3) D. S. Martin, Jr., R. A. Jacobson, L. D. Hunter, and J. E. Benson, *Inorg. Chem.*, **9**, 1276 (1970).

(4) Reviews of such applications are (a) A. S. Davydov, "Theory of Molecular Excitons," translation by M. Kasha and M Oppenheimer, Jr., McGraw-Hill, New York, N. Y., 1962; (b) D. S. McClure, *Solid State Phys.*, **8**, 1 (1959); (c) R. M. Hochstrasser, "Molecular Aspects of Symmetry," W. A. Benjamin, New York, N. Y., 1966, Chapter 10; (d) D. P. Craig and S. H. Walmsley, "Excitons in Molecular Crystals," W. A. Benjamin, New York, N. Y., 1968.

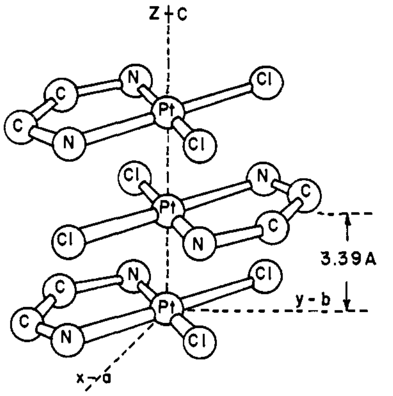

Figure 1. Stacking of molecules of Pt(en)Cl$_2$ in chains along the *c* direction.

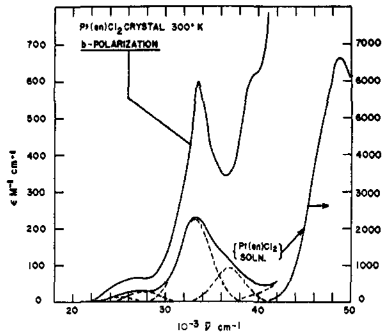

Figure 2. Absorption spectra at 300°K for an aqueous solution of Pt(en)Cl$_2$ and for a single crystal with *b* polarization.

tion have been recognized for regions of high absorption. The single-crystal spectra have also been supplemented by a diffuse reflectance spectrum.

Experimental Section

The Pt(en)Cl$_2$ was prepared by the method of Basolo, Bailar, and Tarr.[5] It was recrystallized repeatedly from solutions in 0.05 *M* HCl which had been saturated at 65°. Crystallization of the compound from 0.05 *M* KCl yielded very thin plates with well-developed faces which, from X-ray diffraction, were found to be 100. The crystals were pale yellow in color and exhibited a distinct dichroism with the higher absorption in the *c* direction. Crystals with an area of 1–2 mm^2 and 1.5–10 μ thick were supported on platinum plates over pinholes of 0.5–0.8-mm diameter. A crystal was attached to the plate by a drop of varnish. These sample plates were then mounted on a light baffle at the slit image in the sample compartment of a Cary 14 spectrophotometer so that light passed through the crystal along the *a* direction. A Glan-type calcite polarizer was inserted in the light beam following the crystal. The polarizer could be rotated by a crank-operated worm gear to attain maximum (*c*) or minimum (*b*) absorption. Simultaneously, a polarizer with identical orientation was placed in the reference compartment beam together with a pinhole and sometimes an absorbance screen as well. Apparently, there was negligible absorption by the crystal from 5500 Å into the near-ir. Absorbance was recorded from 5500 Å through the visible into the uv. A Cary high-intensity source, Model 1471200, was used to 2900 Å and the hydrogen arc was used from 3200 Å to lower wavelengths. Changes in scale of absorbance were atained by changes in the absorber screens in the reference compartment. For each crystal spectrum, a base line was obtained with a pinhole without crystal in each compartment but with the polarizers in place. Absorbance was taken as the difference between the recorded curve and the base line, with adjustment to zero absorbance at 5500 Å.

The maximum angle of convergence in the cell compartment of the Cary spectrophotometer is 9°. The index of refraction n_b was estimated by the Becke line method to be 1.74. Hence, the maximum convergence angle through the crystal was only *ca.* 5°. For a uniform intensity across the beam convergence, the intensity of light with an *a* component of polarization can be estimated as 0.1% of the incident intensity. Hence, this component should not have influenced significantly the *b*-polarized spectra. However, it may have provided some contribution to the eccentricity effects of the polarizer for the high absorption in *z* polarization discussed below.

With *c* polarization, peaks at 25,000 cm^{-1} were recorded without an apparent distortion with indicated absorbances of 3.0–3.4. Therefore, it was concluded that there was no significant "light leak" in this region and the polarizer operates effectively at this wave number. However, it appears that in the uv region at 33,000 cm^{-1} the eccentricity of the polarizer has decreased to a point where 1–2% of light of the crossed polarization is transmitted. Consequently, it was not possible to follow the *c*-polarized (high) absorption above 31,000 cm^{-1}. For the determination of molar absorptivities, crystals of 20–40 μg were weighed on a Cahn electrobalance. Such crystals were about 6 μ thick, and examination of such thick crystals under a polarizing microscope showed they were not of uniform thickness. However, the thinner, more uniform crystals could not be weighed accurately with the balance available to us. The *c* absorbance at 25,000 cm^{-1} with a 6.4-μ crystal was 3.08. The thickness of other crystals was obtained by comparison of this peak with that of the weighed crystals. The crystal spectra reported, however, are for a crystal 1.9 μ thick, where absorption is much lower. From the polarizing microscope it appeared that the quality of this crystal was much superior to that of the weighed standards. General features of these spectra have been duplicated with several specimens. However, values of molar absorbancies are uncertain, possibly by as much as 25% because of nonuniformity of the standards.

To attain low temperatures, the platinum support plates were mounted in a cryostat to which liquid nitrogen and then liquid helium could be introduced. Experience showed that in the cryostat scattering and reflection from the windows, sample holders, and radiation shield gave a "light leak" corresponding to about 0.2%. Therefore, absorbances above 1.5 would contain fairly large errors. However, the details for the thinner crystals would not be badly distorted by this. The large majority of the very fragile thin crystals did not survive cooling to helium temperature. Hence, only room-temperature and liquid N$_2$ (77°K) spectra are reported.

A diffuse reflectance spectrum for a sample of Pt(en)Cl$_2$ was obtained with a Beckman DU spectrophotometer with the appropriate attachment.

Results and Discussion

Solution Spectrum for Pt(en)Cl$_2$. A spectrum of Pt(en)Cl$_2$ in aqueous solution is shown in Figure 2. In the d–d region, from 20,000 to 42,000 cm^{-1}, the spectrum was recorded for a solution which contained 0.318 *M* KCl to suppress aquation. For the region of allowed transitions, $\bar{\nu} > 41,000$ cm^{-1}, the spectrum of a freshly dissolved sample of H$_2$O was used because of interference by chloride ion in this region. The spectrum in the d–d region has been resolved into the four indicated Gaussian components. The location of band maxima, the maximum molar absorbancy, and the indicated oscillator strengths are included in Table I. The spectrum is very similar to that for *cis*-Pt(NH$_3$)$_2$Cl$_2$, although bands are somewhat more intense. The transition assignments for the d–d bands follow those proposed by Chatt, Gamlen, and Orgel.[6] These assignments are also in agreement with the ordering of the d-orbital energies indicated by crystal spectra[7] of K$_2$PtCl$_4$,

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(5) F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Amer. Chem. Soc.*, 72, 2433 (1950).

(6) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

(7) (a) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 4, 1682 (1965); (b) *ibid.*, 5, 1298 (1966).

Table I. Transitions in Pt(en)Cl$_2$ from Solution Spectrum

Wave number, $\bar{\nu}_{max}$, cm^{-1}	Molar absorbancy, ϵ_{max}, M^{-1} 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}	$^3B_2$ ($d_{xy} \leftarrow d_{x^2-y^2}$)	
27,300	31	5.1×10^{-4}	$^3A_2$ ($d_{xy} \leftarrow d_{yz}$)	
			$^3B_1$ ($d_{xy} \leftarrow d_{xz}$)	
33,200	226	4.1×10^{-3}	$^1B_2$ ($d_{xy} \leftarrow d_{x^2-y^2}$)	$x - a$
36,900	94	1.6×10^{-3}	$^1A_2$ ($d_{xy} \leftarrow d_{yz}$)	Forbidden
			$^1B_1$ ($d_{xy} \leftarrow d_{xz}$)	$z - c$
Not observed			$^1B_2$ ($d_{xy} \leftarrow d_{z^2}$)	$x - a$
49,200	6700	2.0×10^{-1}	$^1B_1$ ($d_{xy} \leftarrow L(\pi) - a_2$)	$z - c$
			$^1A_1$ ($d_{xy} \leftarrow L(\pi) - b_2$)	$y - b$
			$^1B_2$ ($d_{xy} \leftarrow L(\pi) - a_1$)	$x - c$
			$^1A_2$ ($d_{xy} \leftarrow L(\pi) - b_1$)	Forbidden

magnetic circular dichroism,[8] and treatments of molecular orbital theory.[9] This ordering of orbitals is shown in Figure 3. Since it is expected that the orbitals for a square-planar molecule should resemble closely those possessing complete D_{4h} symmetry such as PtCl$_4^{2-}$, the z axis for the d orbitals has been chosen as the axis normal to the plane. Pt(en)Cl$_2$ possesses only the symmetry C_2. However, symmetry is approximately C_{2v}, but the mirror operations in the molecule are lost as a consequence of the puckering of the chelate ring. Very likely, the ligand-field contributions to transition intensities will follow closely the constraints of the C_{2v} symmetry. The y axis has been chosen to lie along the molecular symmetry axes. The symmetry designation for the 6p$_z$ orbital, the 5d orbitals, and the ligand π-type orbitals of the chloride ligands under the C_{2v} group are shown in Figure 3. With this choice of axes the x, y, z axes are conveniently directed parallel to the crystallographic axes a, b, c, respectively. It is to be noted that with this choice of axes the d_{xy} orbital is used for σ bonding, so the lowest unfilled orbital in the molecule is the antibonding orbital involving d_{xy}. Also under C_{2v} symmetry the d_{xz} and d_{yz} orbitals, degenerate under D_{4h}, are split. The orbitals shown in Figure 3 include the two lowest unfilled orbitals and the highest filled orbitals which are considered to be the only ones which can be involved in transitions up to the limit of the silica uv, *ca.* 50,000 cm^{-1}. Excited-state assignments for the transitions in the solution spectra, following the orbital assignments of Figure 3, are included in Table I.

The perturbation of the C_{2v} ligand field destroys the center of symmetry and can provide some dipole-allowed character to the d–d transitions. Presumably, this is the cause of the intensity enhancements of bands in the Pt(en)Cl$_2$ solution spectrum, where molar absorptivities are considerably higher than for the corresponding bands of PtCl$_4^{2-}$. The predicted polarizations of the ligand-field dipole excitations are included in Table I. It is especially significant that there will be no ligand-field enhancement of intensity for polarization in the b direction of the crystals for spin-allowed d–d transitions.

The first intense and hence dipole-allowed transition in solution is seen to occur at 49,200 cm^{-1} with an oscillator strength of 0.2. The assignment of this transition is uncertain. Traditionally, the several first-allowed transitions for PtCl$_4^{2-}$ have been assigned as charge transfers, $d_{xy} \leftarrow L(\pi)$,[10,11] although the possibility of an alternative assignment, *viz.*, 6p$_z$ $\leftarrow$ 5d, had been recognized and has been supported recently by Cotton and Harris[9b] and by McCaffery, Schatz, and Stephens.[12]

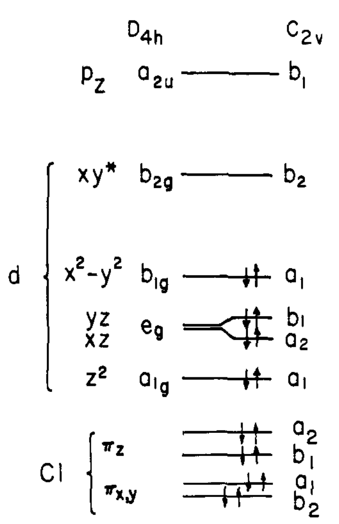

Figure 3. Relative energy of orbitals in Pt^{II} d^8 square-planar complexes. The symmetry properties of the orbitals in the D_{4h} group are indicated together with their correlation with C_{2v} in which the C_2 symmetry axis is directed along the y axis.

There are three allowed transitions $d_{xy} \leftarrow L(\pi)$, as is indicated in Table I, one each with polarizations in directions x, y, and z. Thus the broad band peaking at 49,200 cm^{-1} may include more than one transition and, as seems likely, there may be transitions as well in the region just beyond 50,000 cm^{-1}. The oscillator strength of 0.2 for the band at 49,200 was estimated with the questionable assumption that the band was symmetric. The only nonbonding π orbital for the chlorides is a$_2$ (Cl p$_z$). The transition, $d_{xy} \leftarrow a_2$, which is z polarized, may therefore provide the lowest allowed transition. Evidence will be discussed later to support the presence of a charge-transfer band in this region.

Polarized Crystal Spectrum. A single-crystal spectrum with b polarization, recorded at room tempera-

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[8] D. S. Martin, Jr., J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, **5**, 491 (1966).

[9] (a) H. Basch and H. B. Gray, *ibid.*, **6**, 365 (1967); (b) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 369 (1967).

[10] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1961, p 199.

[11] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, **85**, 260 (1963).

[12] A. J. McCaffery, P. N. Schatz, and P. N. Stephens, *ibid.*, **90**, 5730 (1968).

Table II. Crystal Spectra of $Pt(en)Cl_2$

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

ture, is shown in Figure 2 for comparison with the solution spectrum. It is seen that there is a weak absorption in the region of the solution spin-forbidden d–d bands. There is some red shift apparent in the crystal spectrum, and the molar absorbancy for the crystal is twice as great as for the solution in the region of 25,000 to 29,000 cm^{-1}. However, in the absence of intermolecular interactions, molar absorbancies for polarized spectra of oriented molecules in the crystal must be divided by three for comparison with solution spectra to account for the random orientation of the molecules. At 33,600 cm^{-1}, in the region of the spin-allowed d–d transitions, the absorption is dominated by a fairly narrow, more intense peak which reaches a molar absorbancy of 600 M^{-1}. In addition, there is evidence of a weaker band at about 39,500 cm^{-1} M^{-1}, very close to the minimum in the solution spectrum.

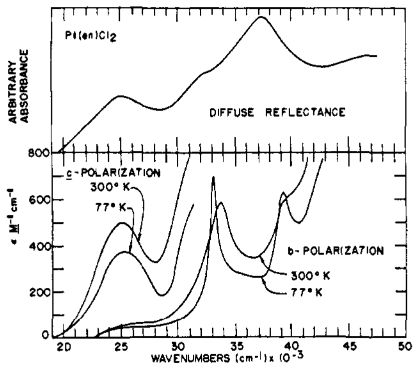

Figure 4. Lower graph, single-crystal spectra for $Pt(en)Cl_2$ at 300°K and 77°K with *c* and *b* polarization. Upper graph, a diffuse reflectance spectrum of $Pt(en)Cl_2$ at 300°K.

The crystal spectra for both *b* and *c* polarization are shown in Figure 4 at both room temperature and at 77°K (liquid N_2). The 33,600-cm^{-1} band in *b* polarization has been reduced in width very significantly at the lower temperature, while the peak has shifted to 33,100 cm^{-1} and has increased in height to 710 cm^{-1} M^{-1}. This peak occurs among some other absorption bands which are not well resolved. This spectrum confirms the earlier report[3] that the band at 33,100 cm^{-1} is not vibronically excited but possesses dipole-allowed character. In addition, the band at 39,100 cm^{-1} has also exhibited a striking increase in peak height at lower temperatures. This band is beyond the range studied in the earlier paper.[3] There are therefore *two* weak but dipole-excited bands in *b* polarization which must be rationalized. Remember that the C_{2v} ligand field gives no enhancement to intensity in this polarization. Characteristics of these two bands are included with the summary in Table II. With the exception of these two peaks, the temperature dependence of the *b* absorption in the region of 24,000–45,000 cm^{-1} indicates that it is vibronically excited.

Throughout the spin-forbidden d–d region, there has been an increase in absorption intensity in *c* polarization by more than 15-fold. There seems to have been some red shift as well, since the onset of absorption is evident at *ca.* 19,000 cm^{-1} compared to 22,000 cm^{-1} for the solution. The maximum at 25,000 cm^{-1} was twice as high as the peak in the spin-allowed d–d bands for the solution. There is a well-defined minimum in the absorption at 28,000 cm^{-1}.

The absorption was too high to follow beyond 31,000 cm^{-1}. It was observed that the polarizer transmits about 1% of light of opposite polarization at 33,000. Hence, a peak reported previously at 33,100 cm^{-1} in *c* polarization was a consequence of the absorption maximum in *b* polarization which was discerned in this cross-polarized light. However, information about the *c*-polarized absorption can be gained from the diffuse reflectance spectrum which is presented at the top of Figure 4. It can be seen that this spectrum follows the crystal *z* polarization spectrum at long wavelengths rather well. There is a shoulder at 34,000 cm^{-1} (the region of the spin-allowed bands and the first anomalous band in the *b*-polarized spectrum). However, there is a maximum at 37,500 cm^{-1}. Furthermore, measurements of specular reflection[13] showed a strong increase in the reflectance as $\bar{\nu}$ was increased above 31,000 cm^{-1}, which indicates a very intense absorption. It was concluded, therefore, that in the crystal spectrum there is an intense dipole-allowed transition or transitions in *c* polarization which provide a maximum at 37,500 cm^{-1}. This intense maximum occurs fairly close to the minimum (40,500 cm^{-1}) in the solution spectrum, and to the minimum in the *b*-polarized spectrum (36,000 cm^{-1}).

Application of Exciton Theory to $Pt(en)Cl_2$. In the orthorhombic unit cell of $Pt(en)Cl_2$ there are four molecules. However, each molecule is related to another in the cell by a *c* face-center translation, and a primitive cell contains only two molecules which are adjacent along the chains. In the crystal spectrum, a Davydov splitting of each excited molecular state into two crystal states might therefore be possible. However, with the parallel alignment of the molecular axes and the uniform molecular spacings along the chains, the intensity of one of the transitions would be zero. Hence, a spectral

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[13] D. W. Lynch, private communication.

transition will appear as a single line equivalent to the situation where each molecule along the chain is translationally equivalent, and a simpler treatment will suffice.

The crystal was first considered to be an aggregate of noninteracting oriented molecules in a rigid lattice, perturbed by the intermolecular interactions. In this treatment[4] the ground-state wave function is the product of the ground-state free-molecule wave functions

$$\Phi^0 = \varphi^0{}_1\varphi^0{}_2\ldots\varphi^0{}_n\ldots\varphi^0{}_m\ldots \quad (1)$$

If molecule m absorbs light and is excited to the state described by φ'_m the localized excitation wave function will be

$$\phi'_m = \varphi^0{}_1\varphi^0{}_2\ldots\varphi^0{}_n\ldots\varphi'_m\ldots \quad (2)$$

From the complete set of localized excitation functions, provided the crystal is large enough for cyclical boundary conditions, a suitable crystal wave function which is a representation of the translation group will be

$$\Phi'_{\mathbf{k}} = N^{-1/2}\sum \exp(\mathrm{i}\mathbf{k}\cdot\mathbf{R}_m)\phi'_m \quad (3)$$

These are the wave functions for Frenkel-type excitons, and they comprise a band of energy states. However, only absorption to the state with $\mathbf{k} = 0$ is allowed in this model, *i.e.*, to the state

$$\Phi'_0 = N^{-1/2}\sum\phi'_m \quad (4)$$

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

$$\bar{\nu}(\Phi'_0 \leftarrow \Phi^0) = \bar{\nu}_0 + D + I \quad (5)$$

where

$$D = \sum_n{}'\Big[\int(\varphi'_m\varphi^0{}_n)^*|V_{m,n}|(\varphi'_m\varphi^0{}_n)\mathrm{d}\tau - \int(\varphi^0{}_m\varphi^0{}_n)^*|V_{m,n}|(\varphi^0{}_m\varphi^0{}_n)\mathrm{d}\tau\Big] \quad (6)$$

and

$$I = \sum{}'I_{n,m} = \sum_n{}'\int(\varphi'_m\varphi^0{}_n)^*|V_{m,n}|(\varphi^0{}_m\varphi'_n)\mathrm{d}\tau \quad (7)$$

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

The quantity D of eq 6 describes the difference in van der Waal's energy between the ground and the excited state. It is usually found to be negative and to provide, therefore, a red shift for the transition energy. Integrals of type I have received considerable attention because they describe the Davydov splittings in crystal spectra. They are frequently evaluated by expanding the potential operator as a transition multipole–multipole interaction with retention of only the first nonzero term. For dipole-allowed transitions with a transition dipole moment $e\mathbf{r}'$, only the dipole–dipole term is retained. With a set of axes in each molecule which places the z axis between centers and common x and y axes orthogonal to z, the value for $I_{n,m}$ becomes

$$I_{n,m} = e^2R^{-3}(\mathbf{x}'_n\mathbf{x}'_m + \mathbf{y}'_n\mathbf{y}'_m - 2\mathbf{z}'_n\mathbf{z}'_m) \quad (8)$$

where $\mathbf{x}'_n$ is the x component of the transition moment r' on atom n, etc.

With Pt(en)Cl_2, the I term for a transition with z polarization centered on the platinum atom provides a shift to lower energy. It will shift a transition with x or y polarizations to higher wave number. Summations over only the two nearest neighbors or over all neighbors in a sphere of 50-Å radius gave substantially equal results. For a 1.0-Å z transition moment, this shift amounts to about $-12{,}000$ cm^{-1}. However, a Pt ← Cl charge-transfer moment should not be centered on the platinum atom. If this moment is centered midway between the platinum and the center of mass of the two chlorine ligands, the value of I is reduced to -6000 cm^{-1}. It is therefore proposed that the intense absorption peaking at 37,500 cm^{-1} is a z-polarized transition, probably charge transfer, which has been shifted from the vicinity of 46,000–53,000 cm^{-1} in the solution spectrum. Since the I term does not account for the complete shift, some contribution must come from the D term and from an influence of the solvent in the solution spectrum as well. The proximity of this intense band enhances the intensity of other absorption bands with c polarization throughout the spin-forbidden d–d region which borrow intensity from it. The temperature dependence of the absorption below 32,000 cm^{-1} indicates that the vibronic excitation mechanism is operative in this region.

Day[14] has commented that the remarkable dichroism and color of bis(dimethylglyoximato)nickel(II), in which similar molecular spacings along chains occur, result from just such an exciton shift of similar magnitude. Also Craig and Hobbins[15] have demonstrated a Davydov shift of 16,000 cm^{-1} in the crystal spectrum of anthracene.

A number of features of the c-polarized spectrum of Pt(en)Cl_2 resemble very closely those of Magnus' green salt (MGS) in which $Pt(NH_3)_4{}^{2+}$ and $PtCl_4{}^{2-}$ ions stack alternately in chains with an ionic separation of 3.24 Å, some 0.15 Å shorter than the spacings for Pt(en)Cl_2 molecules. There is the strong enhancement of spin-forbidden d–d bands with z polarization which is coupled with a red shift. Also, Anex, *et al.*,[16] have shown from specular reflection spectra of MGS that there is an allowed band with z polarization which has been shifted by 8000–12,000 cm^{-1} from solution bands at 42,000 or 46,000 cm^{-1} for the $PtCl_4{}^{2-}$ ion. Presumably, such a shift could be the consequence of transition dipole–dipole interactions between $PtCl_4{}^{2-}$ and $Pt(NH_3)_4{}^{2+}$ to lower the transition energy in $PtCl_4{}^{2-}$. An extended treatment would be required because here there are two molecular species, but similar interactions should occur. For the $Pt(NH_3)_4{}^{2+}$ ion, however, there will be no L(π) orbital and hence the molecular interaction would have to involve the $6p_z \leftarrow 5d_{z^2}$ transitions.

Because of the sign of I given by eq 8, the exciton theory requires strongly allowed transitions with x or y polarizations to appear at much higher energies than the z-polarized transition of similar energy in the free molecule. Such separations for allowed charge-transfer bands can amount to 6000–10,000 cm^{-1} in this crystal. Thus, weak bands at 33,100 cm^{-1} and 39,100 in b polarization are clearly discernible. Since the maximum molar absorbancies of these bands increase upon cooling to liquid nitrogen temperature, the transitions cannot

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[14] P. Day, *Inorg. Chim. Acta Rev.*, 3, 81 (1969).

[15] D. P. Craig and P. C. Hobbins, *J. Chem. Soc.*, 539 (1955).

[16] B. G. Anex, M. E. Ross, and M. W. Hedgecock, *J. Chem. Phys.*, **46**, 1090 (1967).

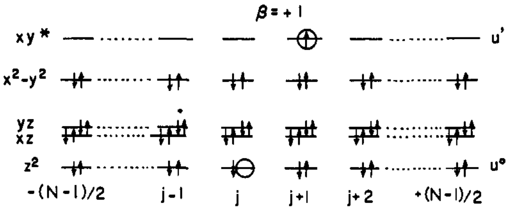

Figure 5. Schematic representation of an ionic excitation, $\phi'_j(+1)$ based on $(d_{xy})_{j+1} \leftarrow (d_{z^2})_j$.

be excited by vibronic means exclusively, but each must contain some dipole moment excitation. An explanation for these transitions must now be sought.

The band at 33,100 cm^{-1} with a maximum molar absorbancy of 600 cm^{-1} M^{-1} at room tempreature very nearly coincides with the maximum in the solution spectrum. In solution this transition was assigned to $d_{xy} \leftarrow d_{x^2-y^2}$. In the solution spectrum of $PtCl_4^{2-}$, the band from this transition has a molar absorbancy of only 60 cm^{-1} M^{-1}. With D_{4h} symmetry for $PtCl_4^{2-}$, the band is completely missing in the z polarization. The ligand field of $Pt(en)Cl_2$ intensifies this transition in the x polarization. It therefore appears plausible that a greater part of the 230 cm^{-1} M^{-1} for ϵ in the solution spectrum is for x polarization. The contribution in the y polarization probably amounts to no more than 40–50 cm^{-1} M^{-1}. With the red shift seen in other bands, this absorption probably falls at 27,000–29,000 cm^{-1}. It is noted that in c polarization, where this band should be very weak, there is a minimum in just this region but no valley occurs in the b-polarized spectrum, where ϵ is *ca.* 65 cm^{-1} M^{-1} at 300°K. Thus the location of a crystal band at just the location of the solution maximum is likely accidental.

Furthermore, the crystal and effective site symmetry prohibit any crystal-field-induced mixing of an allowed y-polarized transition with the x-, z-polarized d–d transitions.

Ionized Exciton States. Since singlet Frenkel-type exciton states could not account for the two bands in b polarization, the interesting possibility of ionized exciton states was considered. The excitation of such states requires a significant overlap of orbitals on neighboring molecules. Therefore, interactions between stacked chains will be neglected and the system can be treated by the simpler theory for one-dimensional systems. An additional simplification will limit excitations to those involving the transfer of an electron from a single filled molecular orbital, u^0, to a single unfilled orbital, u'. Only wave functions involving these two molecular orbitals will be considered. Other electrons in a molecule will be assigned to a core. The N molecules in the chain will be identified by the subscript j which runs from $-(N-1)/2$ to $+(N-1)/2$. As long as only singlet–singlet transitions are treated, an N-electron wave function for the ground state can be defined in an antisymmetrized or determinantal form

$$\Phi^0 = (N!)^{-1/2}|\ldots u^0{}_{j-2}u^0{}_{j-1}u^0{}_j u^0{}_{j+1}u^0{}_{j+2}\ldots| \qquad (9)$$

For a state in which an electron has been excited from the orbital $u^0{}_j$ to $u'{}_{j+\beta}$ the excitation wave function will be

$$\phi'_j(\beta) = (N!)^{-1/2}|\ldots u^0{}_{j-2}u^0{}_{j-1}u'{}_{j+\beta}u^0{}_{j+1}u^0{}_{j+2}\ldots| \qquad (10)$$

This corresponds to a state with a plus charge on molecule j and a negative charge on molecule $j+\beta$. Such an excitation function with $\beta = +1$ has been shown schematically in Figure 5, where u^0 is the d_{z^2} orbital and u' is d_{xy}.

Ionized exciton states for such an idealized linear one-dimensional crystal were treated by Merrifield,[17] who obtained exact solutions for such a system. His treatment describes a molecular exciton or Frenkel band, a series of bound ionic states which are nonconducting, and finally a conduction band of states. It is instructive to examine the limitations imposed by the assumption of his model, and modifications which are needed for a real system.

Merrifield based his treatment upon a single set of excitation functions as are defined in eq 10. The function with a β of zero describes the molecular excitation of the jth molecule in the chain. Merrifield includes as parameters the diagonal matrix elements, $\int \phi'_j(0)|H|\phi'_j(0)d\tau$, and the off-diagonal terms, $\int \phi'_j(0)|H|\phi'_{j'}(0)d\tau$, which involve only the molecular excitation functions and upon which can be based a normal Frenkel exciton

$$\Phi'_k(0) = N^{-1/2}\sum_j \exp(ikj)\phi'_j(0) \qquad (11)$$

The diagonal elements for his ionic states, based on a zero energy for the crystal ground state, were assumed to be

$$\int \phi'_j{}^*(\beta)|H|\phi'_j(\beta) = V(\beta) = \mathrm{IE} - e^2/\epsilon|\beta|R_{j,j+1} \qquad (12)$$

where IE is the energy required to form an electron and hole with infinite separation, ϵ is the bulk dielectric constant, and $R_{j,j+1}$ is the distance between molecules in the chain.

Other off-diagonal matrix elements were taken as those corresponding to the transfer of an electron, ϵ_e, or of a hole, ϵ_h, between nearest-neighbor molecules, *i.e.*

$$\epsilon_e = \int \phi'_j{}^*(\beta)|H|\phi'_j(\beta \pm 1)d\tau \qquad (13)$$

and

$$\epsilon_h = \int \phi'_j{}^*(\beta)|H|\phi'_{j\pm1}(\beta \mp 1)d\tau \qquad (14)$$

The assumption that ϵ_e and ϵ_h are independent of β requires setting them equal to one-electron integrals involving overlap

$$\epsilon_e = \int u'_j|V_{j,j\pm1}|u'_{j\pm1}d\tau \qquad (15)$$

$$\epsilon_h = -\int u^0{}_j|V_{j,j\pm1}|u^0{}_{j\pm1}d\tau \qquad (16)$$

In particular, terms involving two-electron interactions, *i.e.*, $|+e^2/r_{1,2}|$, between electrons on different molecules are neglected. An exact treatment would require inclusion of these terms. However, our consideration will be limited to cases where overlap is not large and these off-diagonal terms are small.

Merrifield's crystal wave functions for the exciton states with k values of zero, the only states which can be optically excited, are

$$\Phi'_0(\beta) = N^{-1/2}\sum_j \phi_j(\beta) \qquad (17)$$

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(17) R. E. Merrifield, *J. Chem. Phys.*, 34, 1835 (1961).

The matrix elements in terms of these functions then become

$$\int \Phi'_0{}^*(\beta)|H|\Phi'_0(\beta)\mathrm{d}\tau = V(\beta) \text{ for } \beta \neq 0 \qquad (18)$$

and

$$\int \Phi'_0{}^*(\beta)|H|\Phi'_0(\beta \pm 1)\mathrm{d}\tau = \epsilon_e + \epsilon_h \qquad (19)$$

The set of ionic functions can be combined into two sets of noninteracting functions defined as

$$\Psi'_+(\beta) = 2^{-1/2}[\Phi'_0(\beta) + \Phi'_0(-\beta)] \qquad (20)$$

and

$$\Psi'_-(\beta) = 2^{-1/2}[\Phi'_0(\beta) - \Phi'_0(-\beta)] \qquad (21)$$

The set $\Psi'_+(\beta)$ interacts with the Frenkel state $\Phi'_0(0)$, whereas the $\Psi'_-(\beta)$ set does not.

Although Merrifield considered only a single set of ionic states based on a set of orbitals, u^0 and u', it is clear that a set of ionic states can be based upon each combination of filled orbital and empty orbitals. In other words, each molecular transition should have a set of excited ionic exciton states. The approximation that the diagonal energy elements are given by eq 12 appears unrealistic, especially for the lowest ionic states, where a bulk dielectric constant is inappropriate. In considering possible ionic states of anthracene and naphthalene, Lyon[18] and Rice and coworkers[19] utilized

$$\begin{aligned} V(1) = {} & \text{(ionization energy, free molecule } u^0) + \\ & \text{(electron affinity, free molecule } u') + \\ & \text{(coulomb energy of ion pairs, } -e^2R^{-1}{}_{j,j+1}) + \\ & \text{(polarization of crystal by dipole)} + \\ & \text{(other smaller terms)} \end{aligned} \qquad (22)$$

The absence of a bulk dielectric constant in the coulombic attraction term should provide for considerably lower energy terms for the $\Psi_+(1)$ and $\Psi_-(1)$ states than Merrifield's function.

In treating optical absorption of linear molecular crystals, Hernandez and Choi[20] limited their considerations to the case where overlap of orbitals between molecules was too small to give appreciable intensities for excitation to the $\Psi'_-(\beta)$ states. The principal intensity in exciting the $\Psi'_+(\beta)$ in that case derived from their mixing with the Frenkel state. For Pt(en)Cl$_2$ the d–d transitions to a $\Phi'_0(0)$ are forbidden in *b* polarization, except for vibronic excitation. Hence transitions to each $\Psi'_+(\beta)$ are forbidden as well. We wish to consider the possibility of sufficient orbital overlap between molecules to permit observation of the transition $\Psi'_-(1) \leftarrow \Phi^0$. The transition moment for these is given as

$$\int \Phi^{0*}|\textstyle\sum r_i|\Psi'_-(1)\mathrm{d}\tau = (2N)^{-1/2} \times$$
$$\left[\sum_j \int u^0{}_j{}^*|\mathbf{r}|u'_{j+1}\mathrm{d}\tau - \sum \int u^0{}_j|\mathbf{r}|u'_{j-1}\mathrm{d}\tau\right] =$$
$$(N/2)^{1/2}[\mathbf{r}'_{j,j+1} - \mathbf{r}'_{j,j-1}] \qquad (23)$$

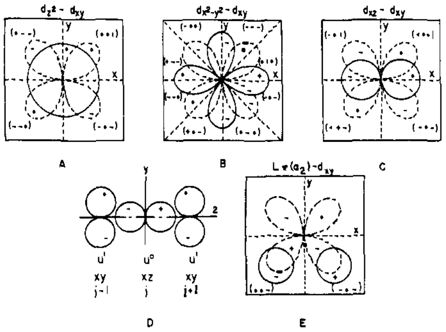

Figure 6. Symmetry properties of the ionic excitation transfer moments $\mathbf{r}_{j,j+1}$ for $\mathrm{d}_{xy} \leftarrow \mathrm{d}$. (A) $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{z^2})_j$; (B) $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{x^2-y^2})_j$; (C) $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{xz})_j$; (D) view of orbitals from along the $+x$ axis involved in $\mathbf{r}'_{j,j+1}$, $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{xz})_j$, and $\mathbf{r}'_{j,j-1}$, $(\mathrm{d}_{xy})_{j-1} \leftarrow (\mathrm{d}_{xz})_j$; (E) $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{L}\pi - \mathrm{a}_2)_j$.

Such a transition dipole moment will be nonzero if

$$\mathbf{r}'_{j,j-1} = -\mathbf{r}'_{j,j+1} \neq 0 \qquad (24)$$

Selection rules for exciting such d–d ionic excitons can be deduced from the sketches in Figure 6. The square in each sketch represents a section midway between the Pt atoms in adjacent molecules *j* and *j* + 1. The outline of the lower orbital, $u^0{}_j$, is solid and that of the excited orbital, u'_{j+1}, is dashed. In each sector in the parentheses are shown the signs of the (*x*, *y*, *z*) components, respectively, of the product $u^0{}_j r u'_{j+1}$, where the origin is taken on the platinum atom of the *j*th molecule. For $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{z^2})_j$ the positive values of *x*, *y*, or *z* components are exactly canceled by negative values in other sectors. Hence, any ionic state transition moment is exactly zero and the transition is dipole forbidden. The same is true for the $(\mathrm{d}_{xy})_{j+1} \leftarrow (\mathrm{d}_{x^2-y^2})_j$ moment. However, for the transition, $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{xz}$, $\mathbf{y}'_{j,j+1}$ is positive in every sector and will therefore be nonzero. The requirement of eq 24, that the dipole moment, $\mathbf{y}'_{j,j+1} = -\mathbf{y}'_{j,j+1}$, is also fulfilled, as can be seen from inspection of Figure 6D. In an exactly similar way the transition from $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{yz}$ will have a nonzero x' transition moment.

The intensity of the ionic exciton transition will depend upon the magnitude of the transition moment, $\mathbf{y}'_{j,j+1}(\mathrm{d}_{xy} \leftarrow \mathrm{d}_{xz})$. An estimate of this transition moment was obtained by numerical integration from the crystal separation of 3.39 Å and the radial d wave function for platinum, utilized by Cotton and Harris[9b] in their molecular orbital treatment of PtCl$_4{}^{2-}$. A value of 0.11 Å was calculated for this moment, $y'_{j,j+1}$, which will provide an oscillator strength of 8.6 × 10^{-3}. The *b*-polarized band at 33,100 cm^{-1} has an observed oscillator strength of only 1.7 × 10^{-3} at 77°K. The calculation is especially crude since the antibonding orbital was treated as pure d_{xy}. However, calculation of transition moments from atomic wave functions typically overestimate intensites for crystal spectra.[4d] However, the calculations indicate that observable intensities should be available for excitation of this ionic state in this crystal, and it seems reasonable to assign the 33,100-cm^{-1} transition to the $\mathrm{d}_{xy} \leftarrow \mathrm{d}_{xz}$ ionic exciton state, $\Psi_-(1)$.

The energy of this ionic transition would be somewhat lower than that of the corresponding spin-allowed molecular excitation at 36,900 cm^{-1} in the solution spectrum.

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(18) L. E. Lyon, *J. Chem. Soc.*, 5001 (1957).

(19) (a) S. L. Choi, J. Jortner, S. A. Rice, and R. Silbey, *J. Chem. Phys.*, 41, 3294 (1964); (b) R. S. Berry, J. Jortner, J. C. Maskip, E. S. Pysh, and S. A. Rice, *ibid.*, 42, 1535 (1965); (c) R. Silbey, J. Jortner, M. T. Vala, Jr., and S. A. Rice, *ibid.*, 42, 2948 (1965).

(20) J. P. Hernandez and S. I. Choi, *ibid.*, 50, 1524 (1969).

It is probably fairly close to the corresponding Frenkel transition energy in the crystal in view of the red shifts on other bands.

Rice[19] and coworkers estimated that such states for anthracene and naphthalene should lie in the vicinity and possibly at lower energy than the allowed Frenkel transition energies. They predicted oscillator strengths for their excitation in the range of *ca.* 10^{-5} from the overlap of π molecular orbitals in these aromatic hydrocarbons. There, the molecular centers were 5.1–5.2 Å apart and only small portions of the MO's, which extended over the entire molecules, overlapped appreciably. Their search for the ionic states at energies below the first spin-allowed Frenkel states failed to reveal any. An anomalous Davydov splitting and intensities of lines in these first Frenkel bands in naphthalene might have resulted from the proximity of ionic states which could mix with the Frenkel states. However, they indicated that evidence concerning the location of the ionic states was inconclusive.

The 33,100-cm^{-1} band seen in the *b* polarization for Pt(en)Cl_2 is in the region where the only possible d–d ionic exciton may logically be expected to occur. The easily observable transition probability for Pt(en)Cl_2, in contrast to the aromatic hydrocarbon, results from the effective alignment of the fairly extended d orbitals on the platinum. Thus its intensity is of the order of the symmetry-forbidden d–d transition. It should be emphasized that in the state $\Psi'_-(1)$ the pair of ions is bound together, and this transition should not lead to photoconductivity which requires sufficient energy to separate the electron from the hole.

It remains to identify the transition at 39,100 cm^{-1} in *b* polarization, since the selection rules provide for only one d–d ionic exciton transition. A transition to $\Psi'_-(2)$ ($d_{xy} \leftarrow d_{xz}$) must have orders of magnitude lower intensity than $\Psi'_-(1)$, since only overlap between nonadjacent molecules contributes to its transition moment. An interesting conjecture is that the 39,100-cm^{-1} band represents excitation to an ionic exciton state based on the charge-transfer transition, $d_{xy} \leftarrow L(\pi)$. An examination of the symmetry of chloride σ and π orbitals reveals that there is only one transition which may have nonzero values for $\mathbf{y}'_{j,j+1} - \mathbf{y}'_{j,j-1}$. This is the a_2 nonbonding π orbital, and therefore a state of the form $\Psi_-(1)$ can be based on $(d_{xy})_{j\pm1} \leftarrow (L(\pi) - a_2)_j$. The symmetry characteristics of its transition moment are evident from Figure 6E. If this assignment for the 39,100-cm^{-1} transition is correct, it is especially interesting because the transition to the Frenkel exciton based on these orbitals is dipole allowed in *z* polarization and is probably a major contributor to the *z*-polarized absorption with maximum at 37,500 cm^{-1}. In this case the transition dipole–dipole interactions have carried the Frenkel state to a significantly lower energy than the ionic state.

A summary of the assignments in the crystal spectra based on the exciton theory with the inclusion of ionic states is presented in Table II. The selection rules and energy predictions from this theory present a coherent rationalization of the observed spectrum. Unfortunately, the spectrum, typical of those for many coordination complexes, is devoid of vibrational structure at the temperatures studied. In view of tentative crystal spectra of some other square-planar complexes of platinum(II), it seems doubtful whether meaningful vibrational structure will be developed even at helium temperatures. However, the orientation of the molecules in this crystal could scarcely be more favorable for obtaining information about molecular polarization and the demonstration of transition selection rules.

One alternative assignment might describe the two *b*-polarized bands as spin-forbidden M ← L charge-transfer bands. These cannot be identified in the solution spectrum. However, if the transition dipole–dipole interactions would shift intense *x* and *y* dipole-allowed transitions to higher energies, the weaker spin-forbidden bands might be discernible. However, no such bands appear in the d–d region for crystals of K_2PtCl_4 and therefore it seems unlikely that the band at 33,100 cm^{-1} could be of this sort. There is perhaps some greater question about the 39,100-cm^{-1} band.

The possibility of measurably intense ionic excitons for this system represents an interesting development for molecular crystal spectroscopy. Related systems therefore deserve further study in order that these assignment proposals can be further tested. There are a number of crystals where planar molecules or ions stack in chains. One of these, already mentioned, is MGS, which, with its related compounds, has been studied by Day, *et al.*,[21] and by Miller.[22] It would be especially interesting to evaluate the temperature dependence of the band polarized normal to the chains in MGS at 24,900 cm^{-1} to determine if its temperature dependence resembles that of the 33,100-cm^{-1} band in Pt(en)Cl_2. Crystal structure determinations by Milburn and Truter[23] for *cis*- and *trans*-$\text{Pt(NH}_3)_2\text{Cl}_2$ have shown stacking of molecules with short Pt–Pt distances in the case of the cis isomer but not for the trans. However, in these cases the crystals belong to the triclinic and monoclinic systems, respectively, and analysis of spectra would not be so straightforward. In addition, Krogman[24] has listed a number of salts of tetracyanoplatinate(II) where anomalous colors are observed with short Pt–Pt distances. However, comprehensive spectral studies in these systems will require the preparation and manipulation of exceedingly thin fragile crystal sections. Future work is likely to be limited by the availability of crystals with suitable form and structure for meaningful study.

Acknowledgment. The authors are grateful for a number of stimulating discussions with Dr. G. J. Small.

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(22) (a) J. R. Miller, *ibid.*, 4452 (1961); (b) *ibid.*, 713 (1965).

(23) G. H. Milburn and M. R. Truter, *ibid.*, *A*, 1609 (1966).

(24) K. Krogman, *Angew. Chem.*, **81**, 10 (1969).