rahedral sites in materials such as ZnS, the observed hyperfine interaction is reduced by 2 orders of magnitude from the normal value.[30] At the moment, we have no means of distinguishing between these alternatives.

Conclusions

At temperatures below 30 K, monomeric Mo(III) complexes based on an octahedral geometry exhibit broad axial or rhombic EPR signals, centered at $g = 4$ and 2. Even with the large line widths, substitution of ^{95}Mo results in significant broadening of the signal with $A_\perp(^{95}Mo)$ on the order of 60 G for Mo(acac)$_3$. This suggests that in enzymes such as nitrogenase[6] and nitrate reductase,[2b,7] which display similar signals but with even narrower lines (due to different relaxation properties of the chromophore), substitution of ^{95}Mo should result in significant broadening or splitting of the signal, if it is indeed due to Mo(III). The failure to observe this effect in the ^{95}Mo-substituted Mo–Fe protein of nitrogenase[2b,9] is therefore further evidence that the characteristic EPR signal is *not* due to a simple Mo(III) site. Assignment of narrow signals at $g \sim 2$, observable at >77 K, to Mo(III) in enzymes containing only isolated molybdenum sites is questionable. Similar signals reported by others[5] for Mo(III) complexes are almost certainly due to polynuclear mixed-valence complexes or monomeric Mo(V) impurities.

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Polarized Electronic Absorption Spectra of (Ethylenediamine)dichloropalladium(II)

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Optical absorption spectra of single crystals of Pd(en)Cl$_2$ are reported for temperatures of 300 and 5 K from 18 000 to 34 000 cm^{-1}. Spectra were recorded for linearly polarized light with the electric vector parallel to the molecular twofold symmetry axis (*b*) and parallel to the stacking of the nearly planar molecules (*c*). In contrast to the corresponding platinum compound, Pt(en)Cl$_2$, the spectra of the Pd(en)Cl$_2$ showed no intensity enhancement whatsoever in the stacking direction of the molecules. Also, there was no evidence in the palladium compound for the intermolecular electron-transfer transitions to ionic states that were observed for the platinum compound. The Pd(en)Cl$_2$ crystal spectra in the measured region were comprised primarily of ligand field bands. Shifts of d–d transition energies from the resolved bands in aqueous solution were determined to be similar to the shifts observed for PtCl$_4^{2-}$ in Magnus' green salt, [Pt(NH$_3$)$_4$][PtCl$_4$].

Introduction

Both Pt(en)Cl$_2$ and Pd(en)Cl$_2$ crystallize with the nearly planar molecules stacked face to face.[1] Earlier, polarized crystal spectra were reported for Pt(en)Cl$_2$.[2] It was shown that an intense, electric dipole allowed transition in Pt(en)Cl$_2$, polarized normal to the molecular plane, had been shifted from 49 000 cm^{-1} where it appears in the solution spectrum to 37 500 cm^{-1} by crystal perturbations. As a consequence, those dipole-forbidden d–d transitions that were polarized in the stacking direction of the molecules were strongly enhanced in intensity. Such behavior is similar to that observed for Magnus' green salt (MGS), [Pt(NH$_3$)$_4$][PtCl$_4$].[3–5] In addition, the Pt(en)Cl$_2$ crystal spectra possessed two bands which were attributed to intermolecular electron-transfer transitions with ionic exciton excited states. The palladium complex has the 4d^8 electronic configuration which is comparable to the 5d^8 of the platinum compound, and the present work provides a quantitative comparison between the spectra of the two compounds.

Experimental Section

Pd(en)Cl$_2$ was prepared by the method of Watt and Carter.[6] Single crystals, prepared by the slow evaporation of aqueous solutions, generally had the form of needles or long, flat platelets. One of the platelets was mounted on a four-circle X-ray diffractometer. A sufficient number of reflections were observed so crystallographic axes could be identified and refined by standard programs. The indicated crystallographic axes and angles were $a = 12.407$ Å, $b = 8.118$ Å, $c = 6.739$ Å, $\alpha = 89.97°$, $\beta = 89.78°$, and $\gamma = 90.00°$. These values were in very satisfactory agreement with the structure reported by Iball et al., viz., orthorhombic C222$_1$, with $a = 8.116$ Å, $b = 12.416$ Å, and $c = 6.736$ Å. Note that we have interchanged the *a* and *b* axes, which have equivalent symmetry, from the convention of Iball et al. in order to retain the convention which was utilized in our earlier spectral study of Pt(en)Cl$_2$. The large faces of the platelets were identified by the diffractometer as (100) with the long dimension or the needle axis being along the *c* axis. For this face the electric vectors for the two transmitted waves are aligned along the *c* axis and along the *b* axis, respectively. Examination of the crystals between crossed polarizers with a quartz wedge indicated that the index of refraction for the *c*-polarized wave (n_c) was less than n_b. The index n_c was found by the Becke line method with a set of index of refraction standard

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Table I. Spectral Components Resolved for Solution of Pd(en)Cl$_2$ in Aqueous HCl

energy ($\bar{\nu}$), cm^{-1}	half-width ($\Delta\bar{\nu}$), cm^{-1}	molar abs (ϵ), cm^{-1} M^{-1}	osc strength^a $\times$ 10^5	transition assignt
23 600 ± 1200	3200 ± 700	16 ± 7	24 ± 12	$^3B_2$, $^3A_2$, $^3B_1$ ← $^1A_1$ (b$_2$, σ^* ← a$_1$, b$_1$, a$_2$)
26 700 ± 100	4000 ± 100	292 ± 18	540 ± 36	$^1B_2$ ← $^1A_1$ (b$_2$, σ^* ← a$_1$, d$_{x^2-y^2}$)
29 400 ± 300	3970 ± 500	105 ± 30	190 ± 59	$^1A_2$, $^1B_1$ ← $^1A_1$ (b$_2$, σ^* ← b$_1$, a$_2$, d$_{yz}$, d$_{xz}$)
34 300 ± 1240	3190 ± 1100	100 ± 70	150 ± 117	$^1B_2$ ← $^1A_1$ (b$_2$, σ^* ← a$_1$, d$_{z^2}$)
39 600 ± 300	5800 ± 700	1490 ± 560	3990 ± 1540	$^1B_1$, $^1B_2$, $^1A_1$ ← $^1A_1$ (charge transfer)

^{a} Oscillator strength = 4.60 $\times$ 10^{-9} $\times$ ϵ $\times$ $\Delta\bar{\nu}$.
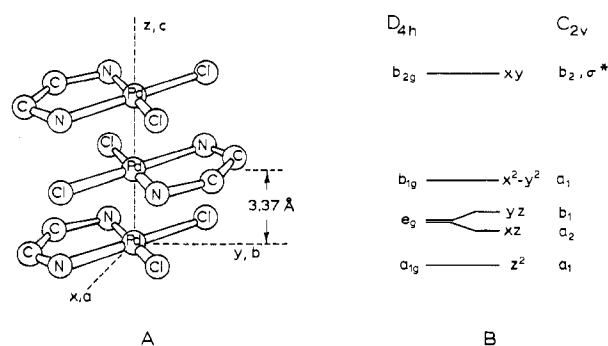

Figure 1. Stacking arrangement of Pd(en)Cl$_2$ molecules along the c axis. Ordering of the d orbitals in square-planar D_{4h} symmetry with the irreducible representations for reduction in symmetry to C_{2v} is applicable to Pd(en)Cl$_2$.

liquids manufactured by the Cargille Corp. to be 1.672 ± 0.001 at 25 °C while n_b was >1.700.

Methods for the measurement of crystal spectra have been described previously.[7] The thickness of one crystal was measured to be 31 ± 1 μ by means of a microscope with a calibrated scale in the eyepiece. The thicknesses of other crystals were determined by comparison of their measured absorbances to the absorbance of this crystal at the same wavelength.

Results and Discussion

Molecular Geometry. The stacking arrangement of Pd-(en)Cl$_2$ molecules along the c axis is shown in Figure 1. The Pd(en)Cl$_2$ molecules possess strictly only C_2 symmetry because of the puckering of the chelate ring; however, the local symmetry at the palladium is essentially C_{2v}. The axes utilized for describing the orbital symmetry are indicated in Figure 1. Thus the axis normal to the plane of the coordinating atoms is retained as the z axis so the molecular y axis becomes the molecular twofold symmetry axis. The irreducible representations for the orbitals upon the reduction in symmetry from D_{4h} to the indicated C_{2v} point group are also shown in the figure.

Aqueous Solution Spectrum. The spectrum of Pd(en)Cl$_2$ in aqueous 0.1 M HCl is presented in Figures 2 and 3. The five Gaussian components shown in the figures provide a very satisfactory fit to the observed spectra. These were determined by the damped least-squares procedure of Paponsek and Pliva.[8] The indicated $\bar{\nu}$, ϵ_{max}, and oscillator strengths (f) for the five components are listed in Table I.

Assignments of the bands for Pd(en)Cl$_2$ have been based upon the assignments for PdCl$_4^{2-}$. However, since there presently is conjecture concerning some d–d transition assignments for PdCl$_4^{2-}$ and the closely related PtCl$_4^{2-}$, consideration of the status of these assignments is needed. For K$_2$PtCl$_4$ at 15 K[7] there are three well-resolved peaks with the indicated maxima $\bar{\nu}$ (cm^{-1}) and polarizations and with molar absorptivities ϵ (cm^{-1} M^{-1}) in parentheses as follows: 20 600 z (10), 20 900 x,y (9); 25 300 x,y (28); 29 800 z (55), 29 200 x,y (37). Since the $^1A_{2g}$ ← $^1A_{1g}$ (b$_{2g}$, σ^* ← b$_{1g}$, d$_{x^2-y^2}$) tran-
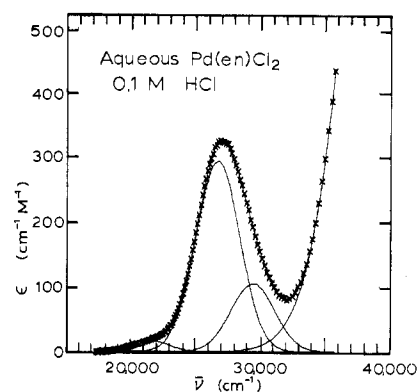

Figure 2. Low-energy absorption spectrum of Pd(en)Cl$_2$ in aqueous HCl. The smooth curve through the plotted experimental points is the sum of the indicated components.
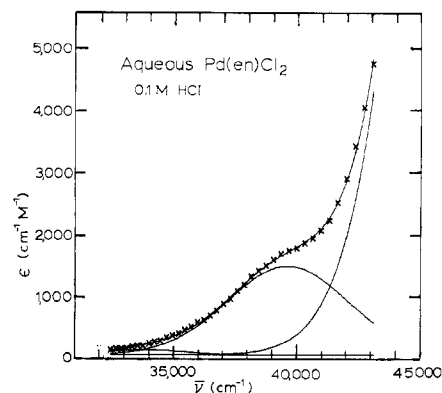

Figure 3. High-energy absorption spectrum of Pd(en)Cl$_2$ in aqueous HCl.

sition is vibronically forbidden in z polarization, there appears no question but that the 25 300-cm^{-1} band corresponds to this transition. (The σ^* is the antibonding orbital utilizing the d$_{xy}$ metal orbital under the choice of axes indicated in Figure 1.) A well-resolved vibrational structure is associated with this band. Also the MCD studies of Martin et al.[9] and Schatz and co-workers[10] for solutions have indicated an A term at 30 300 cm^{-1} so presumably the 29 800–29 200-cm^{-1} band contains the ^1E_g ← $^1A_{1g}$ (b$_{2g}$, σ^* ← e$_g$, d$_{xz,yz}$) transitions.

The question remains about where the $^1B_{2g}$ ← $^1A_{1g}$ (b$_{2g}$, d$_{xy}$ ← a$_{1g}$, d$_{z^2}$) transition lies. We had originally proposed that this transition might correspond to the 20 600–20 900-cm^{-1} band.[11] However, ligand field calculations,[12] which included electron–electron repulsions and spin–orbit coupling with what were considered reasonable Slater–Condon parameters (F_2 and F_4), indicated that the associated $^3B_{2g}$ ← $^3A_{1g}$ (b$_{2g}$, d$_{xy}$ ← a$_{1g}$,

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Table II. Polarized Crystal Spectra for Pd(en)Cl₂ with Resolved Components for 5 K

c-z polarizn			b-y polarizn			
$\bar{\nu}$, cm⁻¹	ϵ, cm⁻¹ M⁻¹	osc strength × 10⁵	$\bar{\nu}$, cm⁻¹	ϵ, cm⁻¹ M⁻¹	osc strength × 10⁵	transition assignt
23 400 ± 1022	40 ± 29	60 ± 50	23 500 ± 160	10 ± 3	17 ± 2	$^3B_2, {}^3A_2, {}^3B_1 \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow a_1, b_1, a_2$)
26 100 ± 280	85 ± 20	126 ± 54	not obsd			$^1B_1({}^1A_2) \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow d_{xz}(a_2), d_{yz}(b_1)$)
28 900 ± 1300	15 ± 26	19 ± 36	28 200 ± 200	149 ± 4	280 ± 10	$^1B_2 \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow a_1, d_{x^2-y^2}$)

d_{z^2}) transitions would be at 12 000–14 000 cm⁻¹ where the observed absorption had fallen far below the expected values for such a transition, in view of the magnitude of the spin–orbit coupling. These computations provided two possibilities about where the $^1B_{2g} \leftarrow {}^1A_{1g}$ transition could fall. It could be close to the $^1E_g \leftarrow {}^1A_{1g}$ and lie under the 29 200–29 800-cm⁻¹ band, or alternatively it could be at ca. 35 300 cm⁻¹. The 20 600–20 900-cm⁻¹ band then would have to arise from a group of spin-forbidden transitions. Weaker spin-forbidden components in both polarizations are evident in the region of 17 000–19 000 cm⁻¹ and at 24 000 cm⁻¹. Since a shoulder at 36 500 cm⁻¹ appears on a rapidly rising absorption in both polarizations,[13] we have generally favored this energy for the $^1B_{2g} \leftarrow {}^1A_{1g}$ ($b_{2g}, \sigma^* \leftarrow a_{1g}, d_{z^2}$) transition. The intensities of the 36 500-cm⁻¹ components are difficult to estimate because they lie on such rapidly rising portions of intense bands; but they perhaps are surprisingly low in comparison to the other spin-allowed d–d transitions. Recently, Elding and Olsson[14] have provided solution spectra for aqueous PtCl₄²⁻ and PdCl₄²⁻ species and their various substituted aquo complexes. They noted that the magnitude of shift for the 37 500-cm⁻¹ band of aqueous PtCl₄²⁻ upon successive replacement of chloride ligands by H₂O resembles the shift of the intense bands rather than the relatively weak d–d bands. Consequently, they have suggested placement of the $^1B_{2g} \leftarrow {}^1A_{1g}$ ($b_{2g}, \sigma^* \leftarrow a_{1g}, d_{z^2}$) transition under the 29 800–29 200-cm⁻¹ band. Also, recently Tuszynski and Gliemann[15] have published results of a new ligand field computation with electron–electron and spin–orbit interactions. They support the assignment of the 20 600–20 900-cm⁻¹ band for the $^1B_{2g} \leftarrow {}^1A_{1g}$ ($b_{2g}, \sigma^* \leftarrow a_{1g}, d_{z^2}$) transition. Their rationalization is based on a much smaller set of Slater–Condon parameters, $F_2 = 410$ and $F_4 = 16$ cm⁻¹ compared to the values used by earlier workers, e.g., $F_2 = 820$ and $F_4 = 54$ cm⁻¹ by Martin et al.,[12] $F_2 = 1406$ and $F_4 = 54$ cm⁻¹ by Patterson et al.,[16] and $F_2 = 1000$ and $F_4 = 100$ cm⁻¹ by Basch and Gray.[17] It appears at present that the $^1B_{2g} \leftarrow {}^1A_{1g}$ transition cannot be considered as unambiguously established.

From the polarized crystal spectra of K₂PdCl₄, reported by Francke and Moncuit[18] and by Rush et al.,[19] it is clear that the d orbitals are not separated as much in energy for the palladium anion as for PtCl₄²⁻. In x,y polarization there is a peak at 21 700 cm⁻¹ with the resolution of vibronic structure. No second peak occurs, but the band tails off on the high-energy side. In z polarization where the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition is vibronically forbidden, the spectrum with no vibrational structure at 15 K peaks at 23 200 cm⁻¹. Also an MCD A term is associated with the broad solution band at 22 000 cm⁻¹ in an aqueous solution.[10] Hence, both groups have assigned the $^1A_{2g} \leftarrow {}^1A_{1g}$ ($b_{2g}, d_{xy} \leftarrow b_{1g}, d_{x^2-y^2}$) transition at 21 700 cm⁻¹ and $^1E_g \leftarrow {}^1A_{1g}$ ($b_{2g}, d_{xy} \leftarrow e_g, d_{xz,yz}$) at 23 200 cm⁻¹. The $^1B_{2g}$

$\leftarrow {}^1A_{1g}$ ($b_{2g}, d_{xy} \leftarrow a_{1g}, d_{z^2}$) transition was considered to be at higher energy. Patterson and co-workers[20] observed a vibrational progression from 27 900 to 29 600 cm⁻¹ in the spectrum of Cs₂PdCl₄ contained in a Cs₂HfCl₆ host crystal which was assigned to this transition to the $^1B_{2g}$ state. However, in neat K₂PdCl₄ crystals there is only very slight absorption from 25 000 to 30 000 cm⁻¹. Elding and Olsson[14] and Tuszynski and Gliemann,[15] however, prefer to place the $^1B_{2g} \leftarrow A_{1g}$ transition in the region of 23 200 cm⁻¹ and consider all the spin-allowed transitions to be closely grouped. The location of the observed bands for crystalline K₂PdCl₄ are shown in Figure 5. We have placed the $^1B_{2g}$ transition at just over 30 000 cm⁻¹. This assignment is enclosed in parentheses, however, because of its uncertainty.

The weak, low-energy component at 23 600 cm⁻¹ for the aqueous solution of Pt(en)Cl₂ is assigned to a group of spin-forbidden transitions that are listed in Table I. This corresponds to a 6600-cm⁻¹ blue shift from the corresponding spin-forbidden band of aqueous PdCl₄²⁻ in accordance with the expected larger crystal field shift of the amine ligand group.

The most intense d–d band for Pd(en)Cl₂ at 26 700 cm⁻¹ is logically the $^1B_2 \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow a_1, d_{x^2-y^2}$) transition. This corresponds to the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition of K₂PdCl₄, identified unambiguously by its strict x,y polarization. It is the most intense of the d–d transitions for PdCl₄²⁻. The transition is blue-shifted by 5900 cm⁻¹ from K₂PdCl₄ to the Pd(en)Cl₂ solution. The transition is electric dipole allowed in x polarization for Pd(en)Cl₂; and it does appear somewhat but not greatly more intense than in K₂PdCl₄, where it is only vibronically allowed. The 29 400-cm⁻¹ band, somewhat weaker than the 26 700-cm⁻¹ band, is then taken as $^1A_2, {}^1B_1 \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow b_1, a_2$). Under the D_{4h} symmetry of K₂PdCl₄ this is a pair of transitions to degenerate ^1E_g states. For C_{2v} symmetry the degeneracy may be broken. The transition to the $^1B_1$ state is dipole allowed in z polarization while the transition to the $^1A_2$ state is dipole forbidden but, of course, vibronically allowed. The blue shift for this band is 7000 cm⁻¹ from K₂PdCl₄.

Although a weak Gaussian component was indicated in the vicinity of 34 000 cm⁻¹, the uncertainties in the parameters indicate that its location and intensities are not given accurately. The assignment of this band is certainly open to question as well. If the $^1B_{2g} \leftarrow {}^1A_{1g}$ ($b_{2g}, \sigma^* \leftarrow d_{z^2}$) transition lies at about 30 000 cm⁻¹ for K₂PdCl₄, then it could be the corresponding transition $^1B_2 \leftarrow {}^1A_1$ ($b_2, \sigma^* \leftarrow a_1, d_{z^2}$), as has been indicated in Table I and Figure 5. It would be dipole allowed in x polarization. However, the assignment as a spin-forbidden ligand-to-metal charge transfer must be considered as a possible alternative.

The intense broad band at 39 500 cm⁻¹ would presumably be $b_2, \sigma^* \leftarrow \pi(Cl)$ charge-transfer transitions. Excited states of $^1B_2, {}^1A_1$, and $^1B_1$ are expected so these would be dipole-allowed transitions with x, y, and z polarizations, respectively. This band is blue-shifted by 3900 cm⁻¹ from PdCl₄²⁻ and is somewhat less intense.

Single-Crystal Spectra. Single-crystal spectra, recorded for c and for b polarizations of Pd(en)Cl₂ at temperatures of 300

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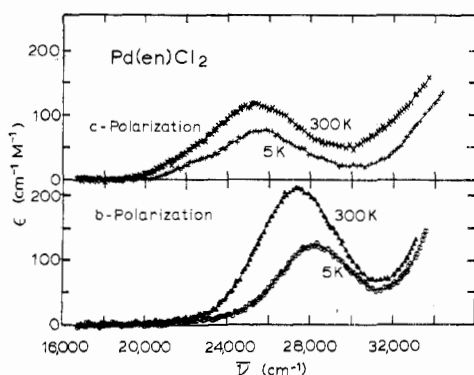
Figure 4. Polarized single-crystal spectra for Pd(en)Cl$_2$ at 300 and 5 K.
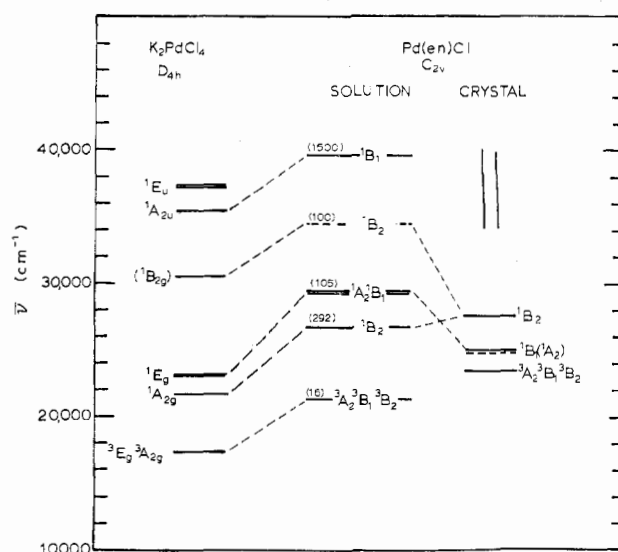

Figure 5. Comparison of corresponding transition energies in single-crystal K$_2$PdCl$_4$[19] and in Pd(en)Cl$_2$ solutions and single crystals.

and 5 K, are shown in Figure 4. Least-squares fits of Gaussian components to the observed spectra were performed, and the components are tabulated in Table II. The maximum in the spectrum of *c* polarization at 5 K was some 2000 cm^{-1} lower in energy than the maximum in *b* polarization. For *c* polarization, in addition to the tail of a high-energy band, the three components listed gave a standard deviation to the fit of 3.2 cm^{-1} M^{-1}. The band at 23 400 cm^{-1} is assigned as spin-forbidden transitions to triplet states which probably include $^3A_2$, $^3B_1$, and $^3B_2$. The major component is the band at 26 100 cm^{-1}, and the parameters of the band at 28 900 cm^{-1} are given with rather high uncertainties. For the *b* polarization, only two components besides the tail of a high-energy band were required to give a standard deviation for the fit of only 2.1 cm^{-1} M^{-1}. This included a spin-forbidden component at 23 500 cm^{-1} and a peak at 28 200 cm^{-1}, very close to the highest energy of the three components in *c* polarization. Hence no component corresponding to the 26 100-cm^{-1} band in *c* polarization was detectable in *b* polarization.

Since the transition $^1B_1 \leftarrow {}^1A_1$ (b_2, $\sigma^* \leftarrow a_2$, d_{xz}) is dipole allowed in *c* polarization, it has been assigned as the 26 100-cm^{-1} band. Although the temperature dependence of the intensity in *c* polarization indicates some vibronic contribution to the intensity of this transition, the temperature dependence is not as great as for the 28 200-cm^{-1} transition in *b* polarization. This assignment indicates a red shift of 3300 cm^{-1} from the $^1B_1$ transition in the aqueous solution species. Such a red shift can be expected as a crystal effect because the transition corresponds to a transition from the d_{xz} orbital with a considerable out-of-plane electron density to the $d_{xy}\sigma^*$ orbital with electron density concentrated in the molecular plane. There will be, therefore, a stronger repulsive interaction with the electrons of neighboring molecules stacked along the *c* axis for the electron in the ground-state orbital than in the excited-state orbital. A comparable red shift of 4000 cm^{-1} was noted in the $^1E_g \leftarrow {}^1A_{1g}$ (b_{2g}, $\sigma^* \leftarrow e_g$, d_{xz}, d_{yz}) transition of MGS. It appears likely, therefore, that the 26 100-cm^{-1} band also includes the $^1A_2 \leftarrow {}^1A_1$ (b_2, $\sigma^* \leftarrow b_1$, d_{yz}) transition as well.

The component at ca. 28 200 cm^{-1} in both the *b* and the *c* polarizations would then appear to be the $^1B_2 \leftarrow {}^1A_1$ (b_2, $\sigma^* \leftarrow a_1$, $d_{x^2-y^2}$) transition. This transition would be dipole allowed in *x*, a polarization which cannot be measured for the (100) faces available on the crystals. The *b* and *c* components are, therefore, only vibronically excited in strict C_{2v} symmetry. The fact that it has the highest intensity is therefore somewhat surprising. However, the corresponding $^1A_{2g} \leftarrow {}^1A_{1g}$ transition in PdCl$_4{}^{2-}$ has a molar absorptivity more than 3 times that of the $^1E_g \leftarrow {}^1A_{1g}$ transitions where only the vibronic mechanism applies for both bands. With these assignments it is seen that the $^1B_2 \leftarrow {}^1A_1$ transition has been blue-shifted by 1500 cm^{-1}. For this transition both orbitals involved are

concentrated in the molecular plane; and very little shift is expected. A small blue shift of the band occurs as the temperature is lowered, which can be seen from Figure 4 and which indeed is normal. For MGS the $^1E_g \leftarrow {}^1A_{1g}$ and the $^1A_{2g} \leftarrow {}^1A_{1g}$ transitions are not resolved but appear as a single peak. This peak corresponds to a 1000-cm^{-1} red shift from the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition of K$_2$PtCl$_4$ single crystals.

The shifts between the corresponding transitions in single-crystal K$_2$PdCl$_4$, Pd(en)Cl$_2$ solution, and Pd(en)Cl$_2$ single crystals are shown in Figure 5. As can be seen from this figure, if the band at ca. 34 200 cm^{-1} in the solution is due to $^1B_2 \leftarrow {}^1A_1$ (b_2, $\sigma^* \leftarrow d_{z^2}$), a red shift of 6000 cm^{-1}, which might be reasonable, would allow it to contribute intensity in the vicinity of 28 000 cm^{-1} as well.

Comparison of the Platinum and Palladium Systems. There is a close similarity in the relationship of the solution spectra for Pt(en)Cl$_2$ and Pd(en)Cl$_2$ to the spectra of the corresponding tetrachloro anion. In each case the solution spectra indicate a blue shift of the d–d transitions in the amine complexes by about 5000–7000 cm^{-1}. There is a greater separation of the bands corresponding to the $^1A_{2g} \leftarrow {}^1A_{1g}$ (D_{4h}) and the $^1E_g \leftarrow {}^1A_{1g}$ transitions of the anions in the platinum complexes than in the palladium complexes. However, the crystal spectra of Pt(en)Cl$_2$ and Pd(en)Cl$_2$ are very dissimilar. First of all, the absorption for *c* polarization had much higher intensity (at least 10 times greater) than *b* polarization for the platinum compound. Indeed, for *c* polarization, the intensity precluded measurements beyond 31 000 cm^{-1} whereas the *b* polarization could be followed to 43 000 cm^{-1}. Diffuse reflectance spectra exhibited a peak at 37 000 cm^{-1} which was apparently a highly allowed transition in *c* polarization. Only the spin-forbidden d–d band could be measured, and its intensity in *c* was 10 times greater than in *b* polarization because of the proximity of the intense transition from which the *z*-polarized transitions can "borrow" intensity. This intense transition at 37 000 cm^{-1} apparently corresponds to an intense band in the PtCl$_4{}^{2-}$ ion at 46 000 cm^{-1}. Anex et al.[21] from specular reflectance spectra of K$_2$PtCl$_4$ have shown a *z*-polarized component at this energy. Molecular excitations in a crystal provide Frenkel-type exciton states. Energy shifts can be estimated from the sum of transition dipole–dipole interactions. With the stacking of planar molecules with the geometry of Pt(en)Cl$_2$, it can be shown[2] that *z*-polarized transitions will be red-shifted and *x*-

(21) Anex, B. G.; Takeuchi, N. *J. Am. Chem. Soc.* **1974**, *96*, 4411.

or y-polarized transitions will be blue-shifted. The magnitude of the shift is proportional to the intensity. This simple model predicts a $12\,000$-cm^{-1} shift for a z-polarized transition with a transition moment of 1 Å e. The theory accounts nicely for the appearance of the shift of the intense transition from $46\,000$ cm^{-1} in PtCl$_4^{2-}$ to $37\,000$ cm^{-1} for Pt(en)Cl₂.

PdCl$_4^{2-}$, in contrast to PtCl$_4^{2-}$, has an intense band at ca. $35\,000$ cm^{-1}. However, crystal spectra have shown that this band is primarily x,y polarized.[18] There is a z-polarized band at $37\,000$ cm^{-1}, and the temperature dependence of the intensity indicates it is electric dipole allowed. However, its intensity is quite low; the oscillator strength is only 7×10^{-3}. There is no other z-polarized component evident below $45\,000$ cm^{-1}. Hence, there is just no high-intensity z-polarized transition in a position to red-shift significantly and affect the z-polarized intensity of dipole-forbidden transitions. This difference between the two elements strongly suggests that the intense bands of platinum are essentially $6p_z \leftarrow 5d$ transitions whereas for palladium they are $d\sigma^*(Pd) \leftarrow \pi(Cl)$. Such a transition must be essentially pure $\sigma^* \leftarrow \pi$ in character. Jørgensen[22] has noted that pure $\sigma^* \leftarrow \pi$ charge-transfer bands normally have low intensity, and the high-intensity charge-transfer transitions invariably possess considerable $\sigma^* \leftarrow \sigma$ character.

The b-polarized spectra for Pd(en)Cl₂ from $20\,000$ to $32\,000$ cm^{-1} were characteristic of a spin-forbidden band and a spin-allowed band, both vibronically excited. This spectrum was quite consistent with the expected d–d transitions appearing as Frenkel-type excitons. In contrast, the b-polarized spectra of Pt(en)Cl₂ are quite different.[2] Although there is the same sort of spin-forbidden vibronic type of band, there are two bands at $33\,100$ and $39\,100$ cm^{-1} whose temperature dependence indicates that they are electric dipole allowed although low-intensity transitions. They were assigned as intermolecular electron-transfer transitions which produced excited ionic exciton states. These bands obscured the intramolecular d–d transitions for Pt(en)Cl₂. The intermolecular electron-transfer bands require overlap of the orbitals of one complex with the b₂, σ^* orbital of the adjacent neighbors. Even though the transitions are electric dipole allowed, the overlap is sufficiently small for the platinum complex that they are of relatively low intensity with oscillator strengths of $(1-2) \times 10^{-3}$. Since the spacing of the palladium molecules match the platinum so closely, comparable transition energies to at least the lowest ionic states might be expected for Pd(en)Cl₂ in the region of the measurable spectrum as well. The absence of such a band in the spectrum of the palladium complex probably results from smaller extension of the d orbitals and the corresponding lower intermolecular overlap than was the case for platinum.

Jensen[23] has reported measurements of circular and linear dichroism by means of a phase modulation spectrophotometer for both Pt(en)Cl₂ and Pd(en)Cl₂. For Pd(en)Cl₂ they indicated that $(A_b - A_c) > 0$ for $\bar{\nu}$ in the range $18\,500$–$22\,700$ cm^{-1} (A_b and A_c are the absorbances for b and c linearly polarized light, respectively), $(A_b - A_c) < 0$ for the range $22\,700$–$25\,600$ cm^{-1}, and $(A_b - A_c) > 0$ for the range $25\,600$–$33\,300$ cm^{-1}. From our linear polarized spectra the absorption is too low below $20\,000$ cm^{-1} for a comparison. However, the c absorption is definitely higher than b from about $21\,000$ cm^{-1} to about $25\,300$ cm^{-1}; and at higher energies A_b is greater than A_c. Hence, Jensen's results are in reasonable agreement with our crystal spectra. However, for Pt(en)Cl₂ Jensen reports a region from $25\,000$ to $31\,000$ cm^{-1} with $(A_b - A_c) > 0$. However, our polarized spectra indicate that A_c is very much greater than A_b for the entire spectroscopically accessible range. Since the linear polarized spectra provide these absorbances in a fairly straightforward manner, the disagreement may result from the involved mathematical resolution of the information from the much more difficult circular dichroism measurements.

The striking differences in the palladium and platinum complexes reveal distinct differences in electronic states and orbital characteristics of the two elements. The high absorption in the stacking direction for Pt(en)Cl₂, which has always been noted as one of the characteristics of Magnus' green salt, apparently results from an intense z-polarized transition at reasonably low energy, which is strongly red-shifted by crystal effects. In addition, the d orbitals of Pt apparently have a greater extension in space than those for Pd since the intermolecular charge-transfer transitions are evident for Pt but not for Pd. Thus, the palladium spectra are those for normal ligand field transitions. However, the spectra of the Pd(en)Cl₂ do indicate shifts in the ligand field excited states which are quite comparable to those which occur in MGS. A number of Magnus-type salts can be prepared from either platinum or palladium complexes, in which the metal–metal spacings are altered by incorporating various substituted amines. The spectra of some of these are presently being investigated.

Registry No. Pd(en)Cl₂, 15020-99-2.

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(23) Jensen, H. P. *Acta Chem. Scand., Ser. A* **1978**, *32*, 156.