complexes, bonding Pt–Cl–Pt, are believed to be formed, the identity of the nonbridging trans ligand of the Pt(IV) reactant clearly has a marked effect on the rate. Electrons have to be accommodated in the d_{z^2} orbital of the Pt(IV) when reduction occurs, and cleavage of the Pt–NH_3 bond is also necessary. Both are more difficult to achieve when the trans ligand is NH_3. The same reasoning is expected to apply for the one-electron outer-sphere reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ with a result that the latter reacts much more slowly. A difference in reduction potentials may also be relevant. Whereas the standard reduction potential for the $PtCl_6^{2-}$–$PtCl_4^{2-}$ couple (in 1 *M* HCl) is known (0.68 V),[21] that for $Pt(NH_3)_5Cl^{3+}$–$Pt(NH_3)_4^{2+}$ does not appear to have been measured. The charge product also favors the reaction of $PtCl_6^{2-}$.

Finally it is appropriate to comment on the Cr^{2+} and V^{2+} reductions of $Pt(NH_3)_5Cl^{3+}$ and the fact that the first but not the second of these reactions proceeds by a 2-equiv change. Chromium(IV) is unstable in aqueous solution and is more difficult to generate than vanadium(IV). Thus with the strong oxidant Tl(III) both Cr^{2+} [22] and V^{2+} [23] undergo 2-equiv changes, but with the milder oxidant Hg(II) only the V^{2+} reductant undergoes a 2-equiv change.[1,3] With $Pt(NH_3)_5Cl^{3+}$ as oxidant the opposite pertains and the mechanism of the reaction appears to be of overriding importance. With Cr^{2+} as reductant the intermediate Pt^{III}–Cl–Cr^{III} is presumably sufficiently long-lived to permit a 2-equiv change. With V^{2+} on the other hand the mechanism is outer sphere, and a 2-equiv change cannot occur within the short lifetime of the outer-sphere adduct involving the two reactants. The results obtained add considerable weight therefore to earlier suggestions that 2-equiv electron-transfer reactions are only tenable if an inner-sphere reaction path obtains.[1,24] At present the only possible exception to this would appear to be the thallium(I)–thallium(III) exchange, which it has been concluded proceeds by a 2-equiv change.[25] On this basis there are grounds for supposing that an inner-sphere mechanism should prevail. However, such a mechanism requires H_2O to function as a bridge for the dominant [H^+]-independent path,[26] and generally H_2O is a poor bridging ligand.[27]

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Registry No. V^{2+}, 15121-26-3; $PtCl_6^{2-}$, 16871-54-8; $Pt(NH_3)_5Cl^{3+}$, 18372-92-4; $Ru(NH_3)_6^{2+}$, 19052-44-9.

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Polarized Crystal Spectra of Potassium Tetrachloropalladate(II) and Potassium Tetrabromopalladate(II)

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Absorption spectra have been recorded for aqueous solutions and single crystals of K_2PdCl_4 and K_2PdBr_4. For both compounds $^1A_{2g}$ and ^1E_g peaks are not resolved in *a* polarization although the $^1A_{2g}$ peak has the much stronger vibrational structure at 15°K. For K_2PdCl_4 the $^1A_{2g}$ and ^1E_g states are assigned at 21,700 and 23,200 cm^{-1}, respectively, and for K_2PdBr_4 they are at 20,200 and 21,700 cm^{-1}. The $^1A_{2u} \leftarrow {}^1A_{1g}$ ($M \leftarrow L\pi$) charge-transfer bands have surprisingly low intensity and are observed at 37,400 and 30,900 cm^{-1} for K_2PdCl_4 and K_2PdBr_4. The $^1B_{1g}$ transition appears to be hidden by the $^1A_{2u}$ transition in the *c* polarization. Weak spin-forbidden bands were observed in both polarizations for both compounds. For K_2PdBr_4 exceptional vibrational structure has been recorded at 15°K. Also, in K_2PdBr_4 two weak transitions at 37,000 and 43,200 cm^{-1} have been assigned as forbidden charge-transfer transitions.

Introduction

Electronic spectra of square-planar palladium complexes in solution have been available for some time.[1-4] In addition, polarized crystal spectra for K_2PdCl_4 were reported by Day et al.[5] and more recently by Francke and Moncuit (FM).[6] These experimental results have provided a stimulus for extensive theoretical treatments of these systems.[7-12] In spite of the numerous studies, controversies about the transition assignments have continued. In the previous experimental work, transition assignments have been based on vibronic and ligand field selection rules. These selection rules for D_{4h} have been recently summarized in a review of square-planar platinum(II) complexes.[13]

The spectral interpretations of K_2PdCl_4 and K_2PdBr_4 have been influenced by earlier investigations of K_2PtCl_4[14,15] and K_2PtBr_4.[16] All of the compounds are isomorphous and the

Table I. Summary of Refractive Index Calculations

	Polarizn	$\bar{\nu}_N$, cm^{-1}	$\lim_{m\to 0}$ $[m\bar{\nu}_0/(\bar{\nu}_M - \bar{\nu}_N)]$	n_N	$10^6(dn/d\bar{\nu})_N$, cm	N	n (Na D)	10^4L, cm
K_2PdCl_4	*c*	18,020	40.4	1.541	3.0	39	1.5389[a]	7.0
	a	17,310	45.0	1.69	13	40	1.68	
K_2PdBr_4	*c*	17,700	51.3	1.579	1.8	50	1.5808[a]	8.9
	a	16,380	60.1	1.79	20	51	1.749	

[a] Determination by Becke line immersion method.

metal atom possesses a d^8 electronic configuration.[17,18]

In the present work, polarized crystal spectra for K_2PdBr_4 are reported, and in addition spectra for K_2PdCl_4 have been obtained over a wider spectral range and with some disagreement with the spectra reported previously.[5,6]

Experimental Section

K_2PdCl_4. Palladium black was oxidized by aqua regia to form H_2PdCl_4. Careful addition of KOH until a pH of 2 was reached permitted the K_2PdCl_4 to crystallize out of solution. Crystals were recrystallized from water and ethanol. A thermogravimetric analysis yielded a weight loss to 580° as Cl_2 of 21.9%, a weight loss to 800° as KCl of 44.4%, and a residue as Pd of 33.7% (calculated values: Cl_2, 21.7%; KCl, 45.7%; Pd, 32.6%).

K_2PdBr_4. Concentrated HBr was added to a solution of H_2PdCl_4 and the mixture was evaporated to dryness; this procedure was repeated. The volume of H_2PdBr_4 solution was reduced before aqueous KOH was added, pH ~2. Red crystallites of K_2PdBr_4 precipitated out of solution. They were filtered and were then washed with cold, absolute ethanol. Thermal gravimetric analysis yielded a weight loss to 525° as Br_2 of 31.9%, a weight loss to 745° as KBr of 47.2%, and a Pd residue of 20.9% (calculated values: Br_2, 31.7%; KBr, 47.2%; Pd, 21.1%).

Refractive Index. Thin crystals of K_2PdBr_4 and K_2PdCl_4 were distinctly dichroic. A determination of the indices of refraction by the Becke line immersion method revealed for K_2PdCl_4 that $n_c(n_E) = 1.5389$ at 25° at the Na D lines and $1.65 < n_a(n_O) < 1.74$ (immersion in 1-bromoaphthalene and CH_2I_2). For K_2PdBr_4 $n_c(n_E) = 1.5804$ and $n_a(n_O) > 1.74$ using the same procedure.

The thickness of a crystal of each compound was determined from the interference of multiple internal reflections of light within the crystal which had *hk*0 faces of high optical quality. The crystals gave well-developed periodic fluctuations (waves) in the absorbance vs. wavelength recording in extended regions of low absorbance. Such interference waves were used previously[16,19,20] to estimate indices of refraction and the thicknesses of crystals. In crystals of K_2PdCl_4 and K_2PdBr_4, the interference effects were of sufficient quality to necessitate revision and improvements in the calculations. The improvements permitted more reliable thicknesses and refractive indices to be obtained.

A minimum in the absorbance waves represents constructive interference of the transmitted and internally reflected light waves. At the minima the crystal thickness is

$$L = N/(2\bar{\nu}_N n_N) \tag{1}$$

where N is the integral number of wavelengths needed to transverse two crystal thicknesses and n_N is the refractive index for the crystal at $\bar{\nu}_N$ in that polarization. The wavelengths can be determined to about ±1–2 Å from slow spectral scans. The wave numbers for the observed minima or maxima were determined and designated as $\bar{\nu}_M$ where M is $N + m$. So, m has integral values for minima and half-integral values for maxima. The variable $\bar{\nu}_M$ was fitted to m by quadratic least-squares. From eq 1 it follows that

$$(N + m)/N = 1 + m/N = n_M\bar{\nu}_M/n_N\bar{\nu}_N = [1 + (\bar{\nu}_M - \bar{\nu}_N)/\bar{\nu}_N][1 + (n_M - n_N)/n_N] \tag{2}$$

From the rearrangement of eq 2

$$m\bar{\nu}_N/(\bar{\nu}_M - \bar{\nu}_N) = N + N[(n_M - n_N)/(\bar{\nu}_M - \bar{\nu}_N)]\bar{\nu}_M/n_N \tag{3}$$

and

$$\lim_{m\to 0}\ [m\bar{\nu}_N/(\bar{\nu}_M - \nu_N)] = N + N(dn/d\bar{\nu})_N\bar{\nu}_M/n_N \tag{4}$$

In eq 4 the limit could be determined rather accurately by linear least squares and it would equal N if the dispersion, $(dn/d\bar{\nu})_N$, were zero. However, it was found that the last term in eq 4 was sometimes greater than 1 so N was not clearly designated without a value for the dispersion.

Equations 1–4 apply for a crystal whose face is perpendicular to the light ray. To determine the appropriate value of N unambiguously, the experiments were extended to include "tilted" crystal data. For uniaxial crystals, such as K_2PdCl_4 and K_2PdBr_4, in which the light ray enters a face which contains the optic axis, the crystals can be rotated in the beam, or "tilted", about the optic axis. Rotation through an angle θ_i results in a shift of the interference maxima and minima to shorter wavelengths. For these conditions, Snell's law applies to both the ordinary and the extraordinary ray, i.e.

$$n = \sin\theta_i/\sin\theta_r \tag{5}$$

The angle of refraction, θ_r, has been shown[16] to be related to the phase delay of the doubly reflected wave by

$$\cos\theta_r = \delta_{\theta_i}/\delta_0 \tag{6}$$

where δ_0 is the phase delay in the untilted crystal, $\theta_i = 0°$. The phase delay can be related to M for tilted and zero rays as

$$\delta_{\theta_i}/\delta_0 = M_{\theta_i}/M_0 \tag{7}$$

It was possible to obtain satisfactory interference waves for incident angle rotations about the optic axis, $\theta_i = \pm 25$–$30°$. Calculation of the refractive index required that m_{θ_i} and m_0 were known at $\bar{\nu}_M$ in addition to N. For the half-integral values of the $m_{\pm\theta_i}$, which occur at minima and maxima of the tilted crystal waves, values of m_0 at the $\bar{\nu}_M$'s were obtained from a quadratic least-squares fit of $\bar{\nu}$ to the integral and half-integral values of m_0. The indices of refraction were then calculated with a number of trial integral values for N below the limit of $m\bar{\nu}_N/(\bar{\nu}_M - \bar{\nu}_N)$. The calculated sets of indices were then fitted by linear least squares to give $n(\bar{\nu}_N)$ and the average dispersion $(\Delta n/\Delta\bar{\nu})$ over the region scanned. For the *c* polarization the values of N were selected which yielded the index of refraction in closest agreement with the value determined by the Becke line method.

Results for the compounds are summarized in Table I. Successive values of N produced changes of about 0.016 in the refractive index. Crystal thicknesses are calculated from values of N, $\bar{\nu}_N$, and n in eq 2.

As a test for consistency in the data, the indicated values of $n(\bar{\nu})$ and $\Delta n/\Delta\bar{\nu}$ were substituted into eq 4 in order to generate a new value of N. In the *c* polarization of K_2PdCl_4, the new N value from eq 4 was 39.0 in exact agreement with the previous value. On the other hand, in the *c* polarization of K_2PdBr_4, the new N was 52.3 in comparison to the previous N of 51. This discrepancy probably reflects the uncertainty in the indicated dispersion; it does appear that the uncertainty in N and therefore in the thickness was probably no greater than ±1–2%.

In the *a* polarization the refractive indices were not obtainable from the Becke line method. Consistency tests were continued for n and $\Delta n/\Delta\bar{\nu}$ until the values of N from eq 4 gave the closest agreement with the trial integral values. In Table I the indicated values of n_a were consistent with the qualitative observation of the Becke line. The higher dispersion in the *a* polarization results from the proximity of strong absorption bands to $\bar{\nu}_N$ and this method appears accurate to within ±0.01 for the index of refraction.

Spectra. Techniques for recording polarized spectra have been previously described.[13,16] The tetragonal structure of both salts is optimal for polarized crystal studies since the $PdCl_4^{2-}$ and $PdBr_4^{2-}$ anions occupy sites of full D_{4h} symmetry. The symmetry axis is directed along the tetragonal *c* axis; hence the *c* or *z* polarization spectrum provides the out-of-plane absorption. The in-plane absorption

Table II. Spectral Components Resolved for K_2PdCl_4

$PdCl_4^{2-}$ aqueous spectrum at 300°K			K_2PdCl_4 crystal spectra at 15°K						
			c-z polarizn			*a*-(*x*, *y*) polarizn			
$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	Transition assignments
15,350	3	2.1×10^{-5}							
17,000	7	7.8×10^{-5}	17,000	1	1.2×10^{-5}				$\left.\begin{array}{l} {}^3A_{2g} \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow b_{2g}\text{-}d_{xy}) \\ {}^3E_g \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow e_g\text{-}d_{xz,yz}) \end{array}\right\}$
						17,700	3	3.3×10^{-5}	
20,820	100	1.4×10^{-3}				21,700	118	9.6×10^{-4}	${}^1A_{2g} \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow b_{2g}\text{-}d_{xy})$
22,440	78	1.75×10^{-3}	23,200	36	4.2×10^{-4}	23,200	30	4.8×10^{-4}	${}^1E_g \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow e_g\text{-}d_{xz,yz})$
30,100	490	7.7×10^{-3}	Not present			Not present			Not $PdCl_4^{2-}$
35,720	9,330	0.17				Intense absorption			${}^1E_u \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow e_u\text{-}L\pi)$
			37,400	388	7.2×10^{-3}	Intense absorption			${}^1A_{2u} \leftarrow {}^1A_{1g}\ (b_{1g}\text{-}\sigma^* \leftarrow b_{2u}\text{-}L\pi)$
40,780	900	1.4×10^{-2}				Intense absorption			
44,980	25,800	0.511				Intense absorption			${}^1E_u \leftarrow {}^1A_{1g}(b_{1g}\text{-}\sigma^* \leftarrow e_u\text{-}L\sigma)$

is provided by the *a* polarization. The *x* and *y* molecular axes are taken to lie along the metal–halogen bonds.

Plots of molar absorptivities vs. wave number were calculated using molar concentrations of 7.051 for K_2PdBr_4 and 8.067 for K_2PdCl_4. Crystal thicknesses were determined by comparison of the absorption peak heights of appropriate bands with the peak heights of the calibrated crystals.

Solution spectra were recorded using the Cary 14 spectrophotometer. Standard solutions were prepared by dissolving the carefully weighed compound in solvents containing 2 *M* NaBr or NaCl. Bromide ion absorbs strongly above 43,000 cm^{-1}, and recording the spectra of $PdBr_4^{2-}$ in pure water was impractical because aquation occurred too rapidly.[21] The spectrum of $PdBr_4^{2-}$ from 25,000 to 44,000 cm^{-1} was obtained with only 0.42 *M* KBr in order to reduce bromide absorption. Components of the spectrum were resolved as lognormals by a least-squares program, LOGFIT.[22] Solution extinction coefficients and oscillator strengths are from components determined by LOGFIT and not the actual tracing.

Results and Discussion

The energy states and the assignment of transitions for the spectral band are discussed in terms of a series of one-electron molecular orbitals. The set of MO's arising from the metal 4d, 5s, and 5p orbitals and the halide p orbitals is shown in Figure 1. The symmetry designations under the D_{4h} group are included. The dashed lines identify the major component of each of the MO's. The ordering of the orbitals follows the calculations of the ground-state orbital energies by the scattered wave–Xα method for K_2PdCl_4 by Messmer, Interrante, and Johnson.[9] The separation of orbitals in Figure 1 are not to exact scale, however. The lowest unfilled orbital is the b_{1g}-σ^* whose principal component is $d_{x^2-y^2}$. The electronic transitions observed below 50,000 cm^{-1} are attributed to excitations from the filled orbitals to the σ^* orbital. Fully dipole-allowed transitions are ${}^1E_u \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_u$-L) in *x*, *y* polarization and ${}^1A_{2u} \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow b_{2u}$-L$\pi$) in *z* polarization. Selection rules for transitions to other electronic states by vibronic coupling have been discussed previously.[13]

In the Xα computations the metal b_{2g} and e_g orbitals were the highest in energy, and the lowest energy transitions might be considered d ← d in character to states with orbital symmetries A_{2g} and E_g. The triplet states for these would lie below the singlet states. However, a feature of the Xα calculations is the proximity of the metal d orbitals and ligand p orbitals with the expectation that the d ← d will fall close to the M ← L charge-transfer transitions.

K_2PdCl_4. In the aqueous solution spectrum in Figure 2, the first maximum lies at 21,000 cm^{-1} with a molar absorptivity of 162 cm^{-1} M^{-1}. This maximum is very broad and was resolved into two components at 20,820 and 22,440 cm^{-1}. Schatz and coworkers observed an MCD *A* component for the solution at 21,100 cm^{-1} so a transition to a degenerate state, presumably ${}^1E_g$ (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$), occurs in this region. Polarized crystal spectra are shown in Figure 3; transition assignments together with the energy of band maxima and intensities for the transitions have been included in Table II.

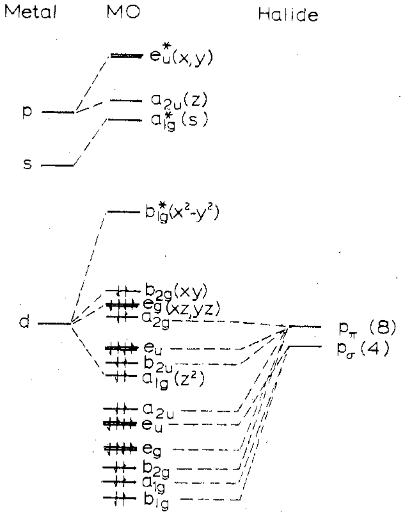

Figure 1. Molecular orbital scheme for a square-planar palladium(II) complex under D_{4h} symmetry. The ordering of the orbital energies, although not to scale, is that calculated by the scattered wave–Xα computation of ref 9. The dashed lines indicate the principal component of each orbital.

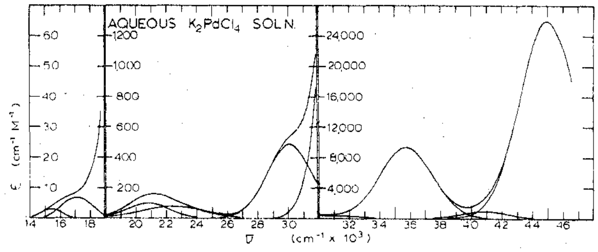

Figure 2. Spectrum of K_2PdCl_4 in an aqueous solution (2 *M* KCl).

At room temperature in the crystal spectra, there were maxima, $\bar{\nu}_{max}$ 21,200 cm^{-1}, ϵ_{max} 250 cm^{-1} M^{-1}, in *a* polarization and $\bar{\nu}_{max}$ 23,000 cm^{-1}, ϵ_{max} 90 cm^{-1} M^{-1}, in *c* polarization. In *a* polarization vibrational structure appeared on the low-energy side of the band but was absent from the high-energy side. No vibrational structure was discernible on the *c*-polarized band. The ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition is forbidden in *c* polarization.[13] It was concluded therefore that the state ${}^1A_{2g}$ (b_{1g}-$\sigma^* \leftarrow b_{2g}$-$d_{xy}$) lies at 21,700 cm^{-1} and that the

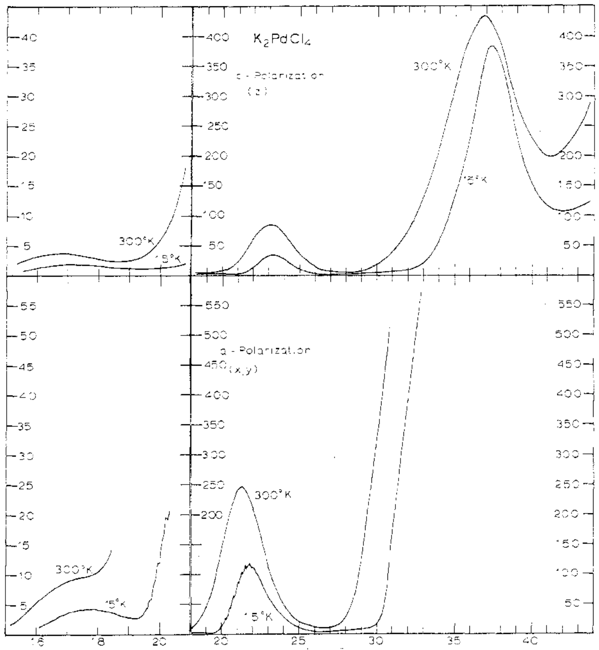

Figure 3. Polarized crystal spectra for K_2PdCl_4. From 15,000 to 20,000 cm^{-1} the crystal thickness was 126 μ; from 18,000 to 29,000 cm^{-1}, 10.5 μ; above 29,000 cm^{-1}, 3.0 μ.

vibrational structure is associated with this transition. The ^1E_g state (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$) has been placed at 23,200 cm^{-1}. Apparently, the two bands in *a* polarization were not resolved at 15°K as was the case for K_2PtCl_4.[14]

As for K_2PtCl_4, vibrational structure was associated with the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition and not the $^1E_g \leftarrow {}^1A_{1g}$ transition. In K_2PdCl_4 the vibrational progression consisted of 12 maxima and 9 poorly resolved shoulders; each shoulder was ca. 120 cm^{-1} below a maximum. The $^1A_{2g}$ transition occurs in the *a* polarization because of vibronic interactions involving vibrations of E_u symmetry.[13] There are two E_u molecular vibrations for $PdCl_4^{2-}$: $\bar{\nu}_6$, primarily a stretching, and $\bar{\nu}_7$, an in-plane bending. The vibrational progressions are consistent with excitation of the maxima by $\bar{\nu}_6$ and the shoulders by $\bar{\nu}_7$. The energy separation between a maximum and its shoulder would be $\bar{\nu}_6 - \bar{\nu}_7$ for the excited electronic state. Thus the separation of 120 cm^{-1}, which applies to the vibrations for the excited electronic states is reasonable in comparison to the ground-state separation of 140 cm^{-1} from $\bar{\nu}_6$ 336 cm^{-1} and $\bar{\nu}_7$ 196 cm^{-1} as reported by Hendra.[23] The separation between successive maxima averaged 264 ± 10 cm^{-1} which can be viewed as the separation of states for the totally symmetric breathing vibration, $\bar{\nu}_1$, in the excited electronic state. Again, the value of $\bar{\nu}_1$ is reasonable in view of the ground-state value of 310 cm^{-1} from the Raman spectrum.[23]

The energy features of the absorption spectra are similar for the $^1A_{2g}$ and ^1E_g states as reported by Francke and Moncuit (FM),[6] who made the same assignments. In contrast, the band intensities are almost 1.5 times higher than theirs. However, the intensities in the spin-forbidden region are quite comparable to those reported by FM.

The absorption between 16,000 and 19,000 cm^{-1} in solution and in the crystals was presumably due to spin-forbidden $\sigma^* \leftarrow d$ transitions to the $^3A_{2g}$ and ^3E_g states. The low intensity of these triplets is consistent with lower spin–orbit coupling for palladium in comparison to platinum. Very faint vibrational structure appeared in the *a* polarization. Further identification of the individual states in the triplets was not feasible.

In the solution spectrum of K_2PdCl_4, there was a component resolved at 30,100 cm^{-1} with ϵ_{max} 490 M^{-1} cm^{-1}. However, absorption in both polarizations was very low in this region. It has been concluded that this component cannot be assigned to $PdCl_4^{2-}$ but rather belongs to a minor solution species.

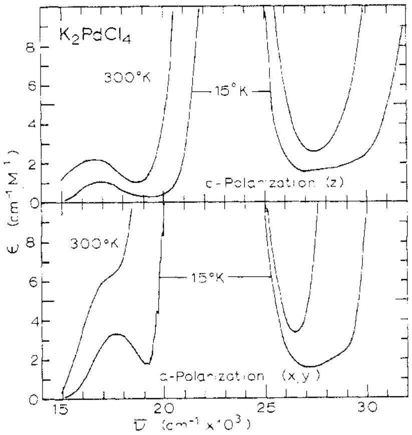

Figure 4. Polarized crystal spectra for K_2PdCl_4. The crystal thickness was 155 μ.

In the crystal from 26,000 to 29,700 cm^{-1} in the *a* polarization and from 26,000 to 31,000 cm^{-1} in the *c* polarization, the absorption was low. Since FM reported a very weak band at 28,500 cm^{-1} in *a* polarization, the absorption of a very thick crystal was measured carefully. Examination of this spectrum in Figure 4 reveals no negative curvature which would indicate a shoulder at 15°K in the *a* scan. In this region the molar absorptivity was only ca. 2–3 cm^{-1} M^{-1}. Any absorption in this region was no more than that in the spin-forbidden $d \leftarrow d$ transition. The minimum was asymmetric and this may be due to the tail of an intense band at higher energies. The presence of a very weak transition cannot be rigorously excluded, however.

FM also reported a transition at 33,000 cm^{-1} in *a* polarization. This transition was based on a shoulder with a molar absorptivity of 130 cm^{-1} M^{-1} which was recorded near the high-energy limit of their scan. Day et al.[5] reported a similar shoulder, $\epsilon \sim 67$ cm^{-1} M^{-1} at 29,500 cm^{-1}. A shoulder in this region was also obtained in our scans with some of the thicker crystals. However, when the thinnest crystals were utilized as shown in Figure 3, it was possible to scan to 33,000 cm^{-1} with only a rapidly increasing absorption to a molar absorptivity of greater than 550 cm^{-1} M^{-1} or nearly twice the peak height of the $^1A_{2g} \leftarrow {}^1A_{1g}$ band at room temperature. It has been our observation that sometimes there is a small depolarization of the transmitted light beam in the crystal. This depolarization probably results from scattering by imperfections of the crystal faces. Hence, for the case of one polarization with very high absorption, the low intensity of light collected may pass through the crystal in the opposite polarization and then suffer such depolarization. As a consequence, where the absorption for this opposite polarization turns upward, a false shoulder appears on the trace. It has been concluded therefore that there is no evidence for a transition to be placed between 29,000 and 33,000 cm^{-1}.

The high-energy solution spectrum of $PdCl_4^{2-}$ is dominated by two intense bands at 35,720 cm^{-1} (ϵ 9330 cm^{-1} M^{-1}) and 44,980 cm^{-1} (ϵ 25,800 cm^{-1} M^{-1}). Since the *c* polarization was scanned to nearly 44,000 cm^{-1} without a molar absorptivity greater than 450 cm^{-1} M^{-1}, it is clear that these two bands must have *x*, *y* polarization and therefore each must be $^1E_u \leftarrow {}^1A_{1g}$. Jorgensen[24] has assigned the lower of the ^1E_u states as primarily b_{1g}-$\sigma^* \leftarrow e_u$-$L\pi$ and the higher energy state as primarily b_{1g}-$\sigma^* \leftarrow e_u$-$L\sigma$. However, there should be some mixing of the e_u orbitals with σ and π character. The relatively high intensity of the lower energy transition (35,720 cm^{-1}) is believed to be a consequence of some mixing of σ character into the e_u orbital of lower energy.

Table III. Spectral Components Resolved for K_2PdBr_4

$PdBr_4^{2-}$ aqueous spectrum at 300°K			K_2PdBr_4 crystal spectra at 15°K						
			c-z polarizn			*a*-(*x*, *y*) polarizn			
$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	$\bar{\nu}$, cm^{-1}	ϵ, cm^{-1} M^{-1}	Osc strength	Transition assignments
			15,700	<1	$\sim 10^{-5}$				
16,210	12	1.3×10^{-4}				16,960	4.8	6.3×10^{-5}	$^3A_{2g} \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow b_{2g}$-$d_{xy}$)
			17,400	<1	$\sim 10^{-5}$				$^3E_g \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$)
						20,200	177	1.1×10^{-3}	$^1A_{2g} \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow b_{2g}$-$d_{xy}$)
20,050	250	4.1×10^{-3}							
			21,730	33	4.1×10^{-4}	22,100	31	3.6×10^{-4}	$^1E_g \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$)
23,450	462	5.3×10^{-3}	Not present			Not present			Not $PdBr_4^{2-}$
26,990	3,700	4.1×10^{-2}	26,990	25	2.5×10^{-4}				$^3E_u \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_u$-$L\pi$)
30,200	10,600	0.16							$^1E_u \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_u$-$L\pi$)
			30,900	550	6.0×10^{-3}				$^1A_{2u} \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow b_{2u}$-$L\pi$)
36,500	5,400	8.4×10^{-2}				Intense absorption			$^3E_u \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_u$-$L\sigma$)
			37,000			Intense absorption			$\sigma^* \leftarrow L$
40,400	28,900	0.56				Intense absorption			$^1E_u \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_u$-$L\sigma$)
			43,200			Intense absorption			$\sigma^* \leftarrow L$

As indicated in Figure 1, there are symmetry-adapted linear combinations of halide π orbitals having b_{2u} symmetry. A transition from this orbital is $^1A_{2u} \leftarrow {}^1A_{1g}$ (σ^*-$b_{1g} \leftarrow b_{2u}$-$L\pi$) which would be *c–z* polarized. The band in the *c* polarization at 37,400 cm^{-1} can be assigned to the $^1A_{2u}$ state. The intensity is quite low for a dipole-allowed transition, and at 15°K the peak height decreases. Jorgensen[24] has noted the low intensity of several transitions which are pure $\sigma^* \leftarrow \pi$ as is this $^1A_{2u} \leftarrow {}^1A_{1g}$. The decrease in intensity at 15°K is not as pronounced as for the d ← d transitions, and possibly vibronically allowed transitions occur in this region also.

The character of the spectra from 20,000 to 24,000 cm^{-1} for K_2PdCl_4 parallels so closely the spectra for K_2PtCl_4 from 23,000 to 30,000 cm^{-1} that a similar assignment for the transitions is indicated. There is the band with well-resolved vibrational structure in only *a* polarization, oscillator strength 9.6×10^{-4} at 15°. Then there are transitions to a degenerate state at 23,200 cm^{-1}, present in both polarizations with oscillator strengths of about 4.0×10^{-4}. The assignment of the transitions in this region to spin allowed d–d transitions is justified, viz., to the $^1A_{2g}$ and ^1E_g states. With the low spin–orbit coupling for palladium, the intensities of these transitions are too great for assignments as transitions to $^3A_{2g}$ and ^3E_g states as Messmer et al.[9] have suggested. In addition, there are lower energy transitions with the expected energies and intensities for these spin-forbidden transitions which are clearly evident in the crystal spectra.

The other low-energy transition predicted by the Xα computation, viz., $^1B_{2g} \leftarrow {}^1A_{1g}$ ($b_{1g}{}^*$-$\sigma^* \leftarrow a_{2g}$-$L\pi$) is vibronically allowed in *a* polarization by virtue of E_u vibrations. On the basis of the molecular vibrations it is forbidden in *c* polarization, although it may receive intensity for this polarization which would certainly be very low by virtue of an A_{1u} lattice vibration. However, this transition corresponds to an electron transfer from a pure $L\pi$ orbital to the σ^*. Since even the fully allowed $^1A_{2u} \leftarrow {}^1A_{1g}$ with such character is rather weak, the transition to the $^1B_{2g}$ state may well be much weaker than the d ← d transitions. It may be hidden under the d ← d or the other charge-transfer bands or it may contribute to the low absorption in the region 26,000–30,000 cm^{-1}. In the present work it is not possible to identify bands which might be assigned to $^{3,1}B_{1g} \leftarrow {}^1A_{1g}$. It appears that the transition to $^1B_{1g}$ must be under the ^1E_u and $^1A_{2u}$ bands.

K_2PdBr_4. The spectrum of K_2PdBr_4 in aqueous solution is shown in Figure 5 which also indicates the resolved component bands. These components have been listed in Table III and they are in good agreement with the tabulations of Jorgensen[2] and McCaffery et al.[3] The first maximum in the spectrum lies at 19,600 cm^{-1}. Its intensity is appropriate for it to be considered a spin-allowed but Laporte-forbidden transition. Schatz and coworkers[3] also observed an MCD *A* term under this band and concluded that it contained the $^1E_g \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$) transition. The crystal spectra for this region are shown in Figures 6 and 7. For *a* polarization there is a peak maximum at 19,800 cm^{-1} with a molar absorbancy of over 400 cm^{-1} M^{-1} at 300°. When the crystal was cooled to 15°K, the intensity of the band was greatly reduced, as expected for a vibronically excited transition. Vibrational structure on the low-energy side of the band was

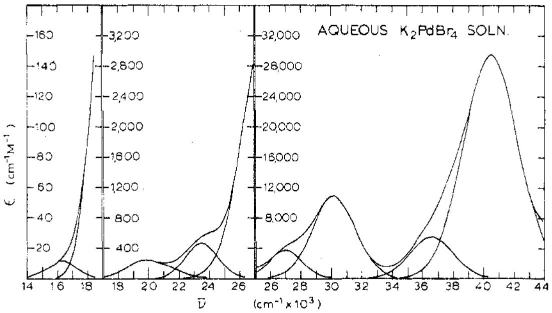

Figure 5. Spectrum of K_2PdBr_4 in aqueous solution. Below 26,000 cm^{-1} the solution was 2 *M* NaBr; above 26,000 cm^{-1}, 0.42 *M* KBr.

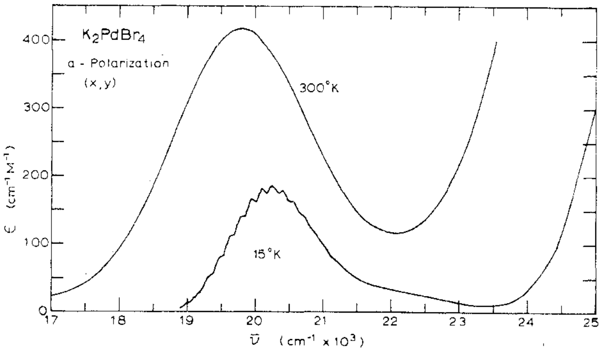

Figure 6. Polarized crystal spectra for K_2PdBr_4; *a*-(*x*, *y*) polarization and 6.8-μ crystal thickness.

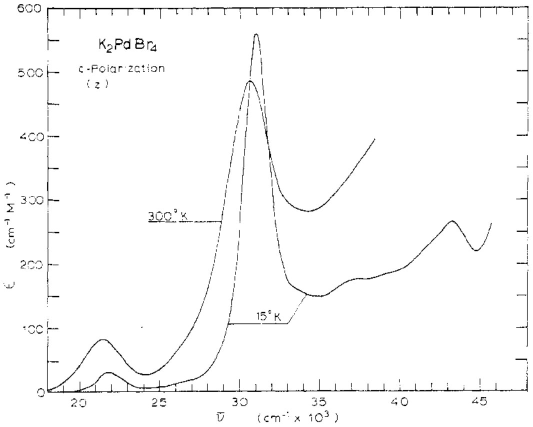

Figure 7. Polarized crystal spectra for K_2PdBr_4; c-z polarization and 6.8-μ crystal thickness.

clearly resolved; and, in addition, a shoulder was discernible at ca. 22,000 cm^{-1}. In c–z polarization the absorption was much weaker, and at 15°K there was a maximum at 22,000 cm^{-1}. These observations appear consistent with assignment of a 21,730-cm^{-1} transition as $^1E_g \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow e_g$-$d_{xz,yz}$) and a 20,200 cm^{-1} transition as $^1A_{2g} \leftarrow {}^1A_{1g}$ (b_{1g}-$\sigma^* \leftarrow b_{2g}$-$d_{xy}$), which is vibronically forbidden in z polarization. Apparently, the transition $^1A_{2g} \leftarrow {}^1A_{1g}$ possesses vibrational structure. The component in the solution spectrum with $\bar{\nu}_{max}$ at 16,200 cm^{-1} has been considered as due to the spin-forbidden d ← d transitions to the $^3A_{2g}$ and ^3E_g states.

Since the absorption was so low in this region, a very thick crystal was required, and polarized spectra for such a crystal are shown in Figure 8. The crystal was sufficiently large to be placed over a 1-mm orifice and the spectrum could be recorded with narrow slit openings for rather high resolution. First, for the c polarization the absorption below 20,000 cm^{-1} is exceedingly low; the molar absorptivity is less than 5 cm^{-1} M^{-1}. However, at 15°K two faint series of vibrational component bands were clearly evident which are barely discernible in the scale of Figure 8. For the first series, centered at 15,700 cm^{-1}, seven peaks were seen with an average separation of 162 cm^{-1}. For the second series, centered at 17,400 cm^{-1} there were nine peaks with an average separation of 166 cm^{-1}. These indicated values for the frequency of the excited state A_{1g} vibrational mode are quite reasonable in view of the indicated value of 192 cm^{-1} in the ground electronic state available from Raman spectroscopy.[25] The wave numbers for the vibration components are listed in Table IV.

Table IV. Vibrational Structure Observed at 15°K for K_2PdBr_4 (cm^{-1})

Spin-forbidden transitions		$^1E_g \leftarrow {}^1A_{1g}$ transition
z polarizn	x, y polarizn	z polarizn
15,240	15,400	20,340
15,410	15,570	20,520
15,580	15,740	20,690
15,730	15,900	20,810
15,910	16,070	20,980
16,060	16,230	21,110
16,220	16,400	21,300
16,770	16,560	21,470
16,930	16,730	21,640
17,110	16,900	21,800
17,270	17,060	21,960
17,430	17,230	22,120
17,610	17,390	22,310
17,780	17,550	
17,940	17,720	
18,100	17,890	
	18,050	
	18,200	
	18,380	

At 15°K it was possible to continue the scan in c polarization to 23,000 cm^{-1} so it included the $^1E_g \leftarrow {}^1A_{1g}$ band as well. Faint vibrational structure was seen in this band as well. On the low-energy side of the band some 13 components are discernible with an average separation of 164 cm^{-1}. This band is excited in c polarization by the vibronic interaction with an E_u vibration. As indicated previously there are two molecular vibrations with this symmetry. Apparently, one of the vibrations is more effective than the other one in the vibronic excitation. However, the poor resolution in part may be due to the contribution from the other vibration. This is the only instance in which any vibrational structure has been detected for this $^1E_{1g} \leftarrow {}^1A_{1g}$ band among the four homologous complexes. Previously, it had been suggested that the absence of structure for the ^1E_g state in $PtCl_4{}^{2-}$ might be due to an equilibrium configuration other than D_{4h}, possibly tetrahedral or D_{2d}.[14] However, this appears not to be the case for $PdBr_4{}^{2-}$.

For a polarization the intensity of absorption was much higher. The shoulder and tail seen below 17,000 cm^{-1} at 300°K were transformed at 15°K into a single progression with a maximum intensity of ca. 5 cm^{-1} M^{-1} at 16,900 cm^{-1}. Hence a single electronic transition is dominant in this region, and this transition is excited mostly by a single vibration. The separation of the clearly seen vibrational components extending from 15,400 to 18,300 cm^{-1} was 165 cm^{-1}. For the spin-forbidden transitions to $^3A_{2g}$, ^3E_g comprising seven excited-state

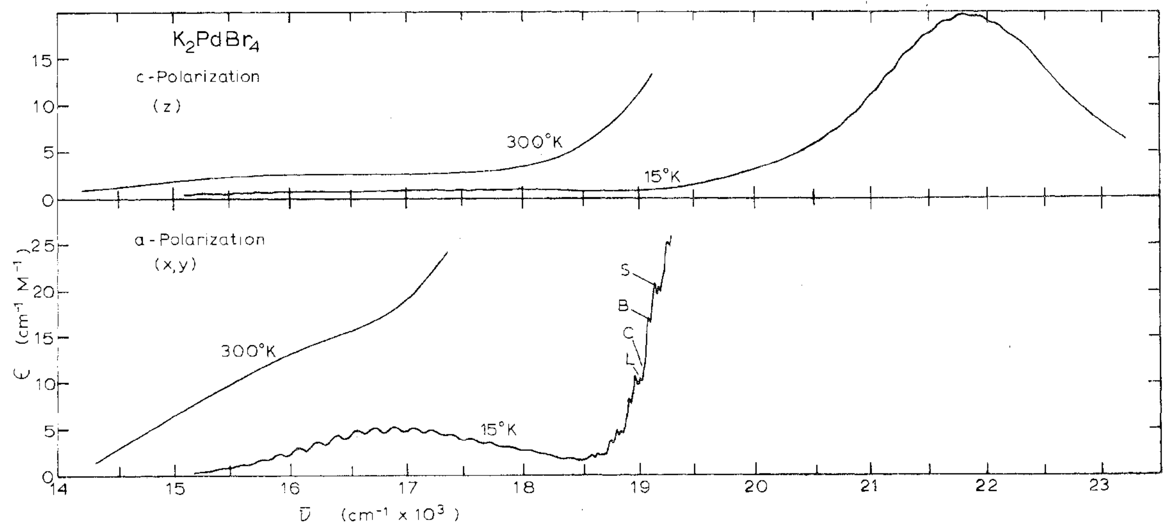

Figure 8. Polarized crystal spectra for K_2PdBr_4. For c–z polarization the thickness was 205 μ; for a-(x, y) polarization, 119 μ.

Table V. Vibrational Structure Observed at 15°K for the $^1A_{2g} \leftarrow {}^1A_{1g}$ Transition of K_2PdBr_4 (cm^{-1})

Resolved components				
L	*B*	*S*	*C*	Maxima
18,520	18,430	18,480	18,570	19,790
18,680	18,590	18,650	18,730	19,950
18,840	18,750	18,800	18,890	20,100
19,000	18,910	18,960	19,040	20,250
19,160	19,080	19,120	19,200	20,400
19,320	19,240	19,290		20,560
19,490	19,400	19,460		20,730
19,640	19,550	19,590		20,880
				21,040
				21,210

energies, only three progressions, the two very weak ones in *c* and this one in *a* polarization, have sufficient intensity to be seen. The four other bands probably have lower intensity although they may contribute somewhat to reduction in the resolution of these three progressions.

In the scans of thick crystals in *a* polarization, the start of the $^1A_{2g} \leftarrow {}^1A_{1g}$ band was observed. These scans for K_2PdBr_4 contained much greater vibrational detail than those for crystals of K_2PtCl_4, K_2PtBr_4, and K_2PdCl_4. As the energy increased, there were groups of four components which were repeated. There were two intense peaks in each group. As can be seen in Figure 7, the strong peak at lower energy has been labeled B and the peak at higher energy has been designated S. A very weak shoulder, labeled C, is on the low-energy side of B and a weak peak, labeled L, is at lower energy than the C shoulder. The wave numbers for the observed components are listed in Table V. The intensities of the C and L bands were too low to have been observed, if present, in the first group where only very weak B and S peaks could be discerned. The corresponding components in the different groups are separated by an average of 160 cm^{-1}. For the $^1A_{2g} \leftarrow {}^1A_{1g}$ band of the crystal in Figure 6, which was recorded with lower resolution, only peaks corresponding to the strongest or S components and at lower energies shoulders arising from the B components could be discerned. However, in thick crystals four complete groups of all the four components were seen. Because the spacing of the components was so regular for these groups, it was concluded that each group corresponded to excitation from a ground state by four different asymmetric vibrational modes. Each member of a group is separated from the corresponding member of the preceding group by $\bar{\nu}_1$, the frequency of the A_{1g} vibrational mode in the excited state. The observation of four vibrational modes was unexpected because a transition to the $^1A_{2g}$ state must be excited by E_u vibrations. There are only the two molecular vibrations mentioned previously, $\bar{\nu}_6$, the asymmetric stretch, and $\bar{\nu}_7$, an in-plane bend with this symmetry. The two strong components S and B have accordingly been assigned to the $\bar{\nu}_6$ and $\bar{\nu}_7$ modes, respectively. The L component might be a lattice vibration; some of these are seen in the infrared spectra at lower energies than $\bar{\nu}_7$. The very weak shoulders, C, may be a combination mode, if a combination includes either $\bar{\nu}_6$ or $\bar{\nu}_7$; then the C component would properly belong to the next lower group of components rather than as they have been designated in Table V and Figure 8.

If these assignments are correct, the difference between S and B components in a group correspond to the difference in the vibrational frequencies $\bar{\nu}_6 - \bar{\nu}_7$ for the excited states. This difference is surprisingly low under this assignment. For the ground-state ions $\bar{\nu}_6$ is 240 cm^{-1} and $\bar{\nu}_7$ is 140 cm^{-1} so the separation is 120 cm^{-1}. Vibrational frequencies are expected to be smaller for the excited electronic state. The indicated $\bar{\nu}_1(A_{1g})$ is 164 cm^{-1} for the excited state whereas it is 192 cm^{-1} in the ground state from the Raman spectrum. Since this is a stretching frequency, a similar decrease in the stretching mode seems likely. However, for the difference in $\bar{\nu}_6 - \bar{\nu}_7$ to decrease from 120 to 50 cm^{-1}, $\bar{\nu}_7$ would have to be no smaller in the excited state and perhaps even slightly larger than in the ground state. Such an increase would indicate that the E_u bending vibration in the excited state with the expanded bonds receives some resistance from its neighbors. The bending displacements do decrease the Br–K distances much more rapidly than stretching vibrations. In the infrared spectrum there is a lattice vibration observed at 85 cm^{-1} which is 140 cm^{-1} below the $\bar{\nu}_6$. The difference between L and S of 123 cm^{-1} appears reasonably consistent with this number. Other assignments of the components were considered but none was believed as satisfactory as the one described.

It can be seen that the absorption for both polarizations in the crystal is very low in the vicinity of 23,000 cm^{-1}. Hence the shoulder resolved as a band with ϵ 400 cm^{-1} M^{-1} from the solution spectrum should not be attributed to $PdBr_4^{2-}$ but rather probably arises from a minor solution species.

At high energies the solution spectrum of $PdBr_4^{2-}$ is dominated by intense peaks at 30,200 cm^{-1}, ϵ 10,600 cm^{-1} M^{-1}, and 40,400 cm^{-1}, ϵ 28,900 cm^{-1} M^{-1}. Since the absorption in *c–z* polarization of the crystal is quite low, 600 cm^{-1} M^{-1}, out to 47,000 cm^{-1}, these intense bands must each be ^1E_u. In agreement with Jorgensen[24] we are assigning these transitions as $b_{1g}\text{-}\sigma^* \leftarrow e_u\text{-}L\pi$ and $b_{1g}\text{-}\sigma^* \leftarrow e_u\text{-}L\sigma$, respectively. However, as with $PdCl_4^{2-}$, the lower energy transition must gain considerable intensity by some mixing of π and σ character in the two e_u orbitals. Each of the two intense bands in solution have shoulders on the low-energy side, at 26,900 cm^{-1}, ϵ 3700 cm^{-1} M^{-1}, and at 36,500 cm^{-1}, ϵ 5400 cm^{-1} M^{-1}. Again, these must occur in the *x*, *y* polarization. These are attributed to transitions to ^3E_u states. Such shoulders are frequently seen in charge-transfer spectra of bromide and iodide complexes and they occur by virtue of spin–orbit coupling of the halide orbitals. Such coupling mixes the ^1E_u states, which in the D_4' double group have E_{1u}' symmetry, with the E_{1u}' components of the ^3E_u states of D_{4h}. Hence, the $^3E_u \leftarrow {}^1A_{1g}$ transitions borrow intensity for *x*, *y* polarization. Such shoulders are apparently not seen for the $PdCl_4^{2-}$ ion because the spin–orbit coupling of chlorine is so low.

In the high-energy region the spectrum in *c–z* polarization is dominated by the single peak, which grows taller as it narrows at lower temperature. This transition, with a $\bar{\nu}$ of 30,900 cm^{-1} and ϵ of 550 cm^{-1} M^{-1} at 15°K is therefore dipole allowed and can be assigned to excitation to the $^1A_{2u}$ state ($b_{1g}\text{-}\sigma^* \leftarrow b_{2u}\text{-}L\pi$). It has relatively low intensity in contrast to the ^1E_u transitions and is consistent with the feature that the b_{2u} orbital has pure π character. However, it does occur very close to the lower energy $^1E_u \leftarrow {}^1A_{1g}$ band of the solution.

There is evidence for a weak transition in *c–z* polarization at 26,920 cm^{-1}, ϵ_{max} 21 cm^{-1} M^{-1}, which is even weaker than the $^1E_g \leftarrow {}^1A_{1g}$ component in this polarization. The assignment of this transition is uncertain. Admittedly, it might be the transition to $^1B_{1g}$ state ($b_{1g}\text{-}\sigma^* \leftarrow a_{1g}\text{-}d_{z^2}$). However its proximity in energy to the $^3E_u \leftarrow {}^1A_{1g}$ transition in *x*, *y* polarization suggests that it may be another component of this transition. Other low-intensity transitions appear at higher energy as well. There appears to be a rather general absorption above 34,000 cm^{-1} which might be due to a number of $b_{1g}\text{-}\sigma^* \leftarrow L\pi$ transitions. There is a minor peak at 37,000 cm^{-1}. The fairly distinct peak at 43,200 cm^{-1} might correspond to the $^1A_{1g}$ or $^1B_{1g}$ arising from $b_{1g}\text{-}\sigma^* \leftarrow b_{1g}$ or $a_{1g}\text{-}L\sigma$. Absolute intensites are uncertain because of the tail of a more intense band lying beyond the region of experiment.

Comparison of the Platinum and Palladium Salts. The energy states for K_2PdCl_4 and K_2PdBr_4 are shown for comparison in Figure 9. For both salts the separation of the

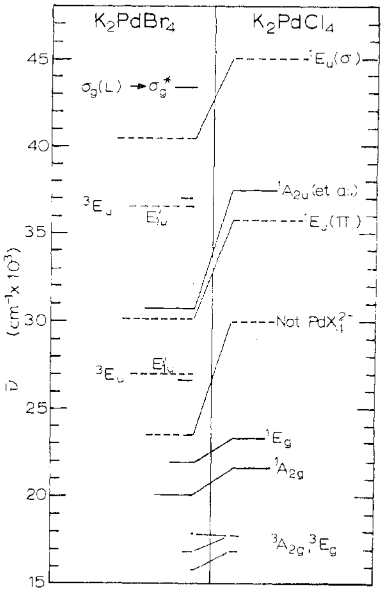

Figure 9. Comparison for excited states of K_2PdCl_4 and K_2PdBr_4. The length of the line for each state is proportional to log ϵ from the crystal spectra at 15°K. The dashed lines are proportional to log ϵ from the solution spectra.

$^1A_{2g}$ and ^1E_g states is less than 2000 cm^{-1} so the corresponding spectral bands are not clearly resolved in a–(x, y) polarization at 15°K. For the corresponding platinum salts this difference is greater than 2500 cm^{-1}. It is so great indeed in K_2PtCl_4 that two maxima occur in x, y polarization even at 300°K. Two maxima are resolved for K_2PtBr_4 at 77°K. Since this separation reflects differences in the π-antibonding character of the d_{xy} and the $d_{xz,yz}$ orbitals, the result indicates somewhat greater π bonding for the platinum complexes. The $^1A_{2g}$ and ^1E_g states for K_2PdBr_4 lie not more than 1500 cm^{-1} below those for K_2PdCl_4. This result is in accordance with the well-recognized weaker ligand field for bromide. The corresponding difference is somewhat greater for the platinum salts, averaging 2100 cm^{-1}.

Solutions of K_2PdCl_4, K_2PdBr_4, and K_2PtBr_4 all have absorption bands of intermediate intensity, ϵ's of ca. 400–600 cm^{-1} M^{-1} at energies where there are virtually no absorptions greater than ca. 50 cm^{-1} M^{-1} for the crystals. Since there is generally good correlation between energies of other transitions between crystals and solutions, these anomalous bands have been assigned to minor solution species. For each of these systems it is possible to form crystals of salts with the dimeric anion, $M_2X_6^{2-}$. Solution spectra for each of these salts in suitable solvents[4,26] have shown intense bands in this region. The $M_2X_6^{2-}$ ions therefore appear to be likely candidates for these minor solution species. For the Pt–Cl system where the dimeric species are least stable, no such anomalous absorption was evident in the solution.[14]

The two ^1E_u and the $^1A_{2u}$ states for K_2PdBr_4 lie from 4500 to 6500 cm^{-1} lower than for K_2PdCl_4. This fairly large separation is consistent with their assignment as $\sigma^* \leftarrow$ L charge transfers.

Katô[8] has proposed an alternative assignment from the present one. His assignment was based on the signs for the MCD A terms associated with the two intense bands in solutions of K_2PdCl_4 and K_2PdBr_4. This assignment required the actual molecular wave functions. He employed wave functions obtained from semiempirical SCF molecular orbitals constructed from Slater-type orbitals for the $PdCl_4^{2-}$ ion. His computations indicate that the sign of the MCD A term for b_{1g}-$\sigma^* \leftarrow e_u$-Lπ is opposite from that for the b_{1g}-$\sigma^* \leftarrow e_u$-Lσ and a_{2u}-$p_z \leftarrow e_g$-$d_{xz,yz}$ transitions. The intense solution band with the higher energy (45,000 cm^{-1}) possessed the sign which he calculated for the b_{1g}-$\sigma^* \leftarrow e_u$-Lπ transition. Since $\sigma^* \leftarrow$ Lσ must occur at still higher energy, the lower energy $^1E_u \leftarrow {}^1A_{1g}$ transition must then be assigned as a_{2u}-$p_z \leftarrow e_g$-$d_{xz,yz}$. However, this order was not in agreement with his calculated orbital energies. Also, if the a_{2u}-$p_z \leftarrow e_g$-$d_{xz,yz}$ transition were to occur at so low an energy, then the absence from the c–z polarized spectrum of the transition $^1A_{2u} \leftarrow {}^1A_{1g}$ (a_{2u}-$p_z \leftarrow a_{1g}$-d_{z^2}) is most puzzling. This transition should be very intense, and there is no evidence for such an intense transition below 48,000 cm^{-1} for K_2PdBr_4 or below 45,000 cm^{-1} for K_2PtCl_4. On the other hand the low-intensity but dipole-allowed transition at only 30,900 cm^{-1} is consistent with a ligand to metal charge transfer.

K_2PtCl_4 presents a somewhat different scheme of energy states for the other three salts. There are no intense transitions to ^1E_u states far below a comparably intense transition to an $^1A_{2u}$ state. However, the absorption in K_2PtCl_4 crystals clearly indicates strong absorption in both polarizations between 40,000 and 50,000 cm^{-1}. This feature is confirmed by the specular reflectance measurements of Anex and Takeudhi[27] which indicate a band of much higher intensity in c–z polarization at 46,300 cm^{-1} than the absorption in a–(x, y) polarization. The intense transitions in K_2PtCl_4 may well be largely of $p_z \leftarrow$ d character. In K_2PtBr_4 it was shown[16] that although the lower intense transition is primarily charge transfer, the higher bands are probably of a mixed character. However, the spectra of the palladium salts indicate that the observed intense high-energy bands are all essentially of charge-transfer character.

Registry No. K_2PdCl_4, 10025-98-6; K_2PdBr_4, 13826-93-2.

References and Notes

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