

Allowed Quartz-Ultraviolet Transitions of the Tetrachloro Complexes of Platinum(II) and Palladium(II)^{1a}

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Abstract: The polarized single-crystal reflection spectra and the corresponding absorption spectra derived from them *via* Kramers–Kronig analyses are reported in the 16- to 47-kK region for K_2PtCl_4 and K_2PdCl_4 . These spectra and the conclusions drawn from them illustrate the importance of using polarization data to assist in establishing the correlations that exist between the transitions that are observed in related systems. It is thus found that, contrary to the implications of the generally accepted spectral assignments for these compounds, the lowest energy allowed electronic transition of $PtCl_4^{2-}$ and the corresponding transition of $PdCl_4^{2-}$ display markedly different polarization behavior. In particular, the 46-kK band of K_2PtCl_4 contains substantial out-of-plane intensity, which is interpreted in terms of a relatively low-lying $PtCl_4^{2-} 5d_{z^2} \rightarrow 6p_z$ transition. The predominantly in-plane polarization of the $PdCl_4^{2-}$ transitions is, on the other hand, consistent with the ligand-to-metal assignments currently associated with them. The relationship of the out-of-plane $PtCl_4^{2-}$ assignment to previous work on the Magnus-type salts and other implications of the assignments made here are explored.

A previously reported study of the single-crystal spectra of Magnus' green salt and its methyl and ethyl analogs² produced evidence that the colors of these substances are closely related to a strong out-of-plane ultraviolet band whose energy is highly sensitive to the perturbation experienced in the crystal by the component ions. This band was taken to be derived from that observed at 46.3 kK in $PtCl_4^{2-}$ aqueous solution, an identification which suggests the experimental verification of the out-of-plane polarization that is thus required for the $PtCl_4^{2-}$ transition. Moreover, the extension of such polarization studies to such closely related systems as $PdCl_4^{2-}$ holds the promise of providing additional evidence for the characterization of the transition involved here and thus putting one in a position to understand in more detail the interesting solid state effects noted in the Magnus' salts² and other planar systems.^{3–5}

Polarization studies of the intense ultraviolet transitions of such systems as $PtCl_4^{2-}$ and $PdCl_4^{2-}$ are also of significance relative to the considerable effort that has been put forth to understand the electronic structures of planar complexes as such.⁶ Much of this work has centered on the often Laporte-forbidden, and at best weakly allowed, $d \rightarrow d$ transitions, probably because of the large amount of carefully obtained experimental data that has accumulated for them. The identity of the more intense bands in the spectra of these compounds can, however, have an important bearing on this problem. It will be noted, for instance, that the determination of the polarization of thoroughly allowed bands leads one to the symmetry of the associated

excited states in a much more direct manner than is the case for $d \rightarrow d$ transitions, where to make such an identification one has to invoke vibronic-coupling arguments.⁷ Moreover, in at least one instance,^{6a} the identity of the first allowed band has played a significant role in the parameterization of a semiempirical theory for planar complexes.

The application of the techniques of reflection spectroscopy makes feasible the study of the polarized crystal spectra of bands whose intensities render impractical their study in direct absorption.^{2,3,5} In the presently reported work, therefore, polarized single-crystal reflection spectra have been obtained for K_2PtCl_4 and K_2PdCl_4 . These spectra and the absorption spectra derived through the application of the Kramers–Kronig transform to the reflection data have provided significant new evidence relative to the identity of the allowed transitions in the d^8 square-planar halides. The conclusions thus reached have provided a gratifying confirmation of the interpretation presented previously for the Magnus' green salt results² and the closely related solid state phenomena noted in the d^8 glyoximates.³ They have, moreover, also provided significant new information relative to current interpretive models for planar complexes.

Experimental Section

Preparation and Purity of Crystals. Previous studies,^{9–15} veri-

(1) (a) The work reported here has been partially supported by the National Science Foundation and the National Institutes of Health and was presented in preliminary form at the Ohio State Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, September 1968. (b) Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La. 70122. (c) On leave from Tokushima University, Tokushima, Japan, 1966–1967.

(2) B. G. Anex, M. E. Ross, and M. W. Hedgcock, *J. Chem. Phys.*, **46**, 1090 (1967).

(3) B. G. Anex and F. K. Krist, *J. Amer. Chem. Soc.*, **89**, 6114 (1967).

(4) P. Day, *Inorg. Chim. Acta Rev.*, **3**, 81 (1969).

(5) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).

(6) See, for instance: (a) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 365 (1967); (b) F. A. Cotton and C. B. Harris, *ibid.*, **6**, 369 (1967).

(7) Illustrations of the complications that can arise in applying vibronic coupling arguments to the assignment of $d \rightarrow d$ transitions are provided by: (a) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, **4**, 514 (1965); (b) D. S. Martin, Jr., M. A. Tucker, and A. J. Kassman, *ibid.*, **4**, 1682 (1965).

(8) (a) B. G. Anex, *Mol. Cryst.*, **1**, 1 (1966); (b) L. J. Parkhurst and B. G. Anex, *J. Chem. Phys.*, **45**, 862 (1966).

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

(10) S. C. Srivastava and L. Newman, *Inorg. Chem.*, **5**, 1506 (1966).

(11) C. K. Jørgensen, "Absorption Spectra of Complexes of Heavy Metals," Report to U. S. Army, Frankfurt am Main, October 1958.

(12) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley, Reading, Mass., 1962.

(13) A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, **90**, 5730 (1968).

(14) C. M. Harris, S. E. Livingstone, and I. H. Reece, *J. Chem. Soc.*, 1505 (1959).

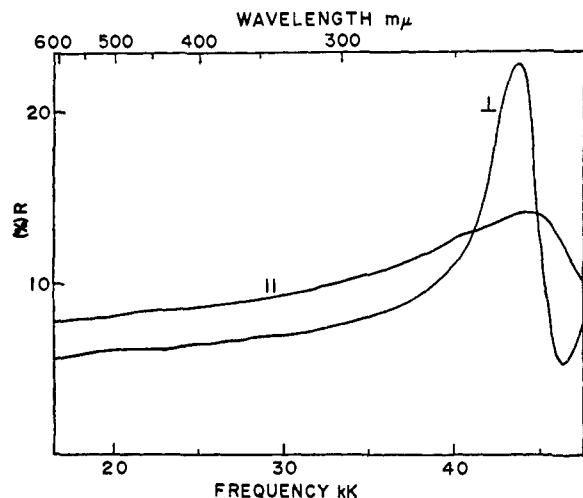


Figure 1. Polarized reflection spectra for a side face (*i.e.*, a face in the $(hk0)$ zone) of the K_2PtCl_4 single crystal. The curve labeled \perp is that obtained when the electric vector of the incident radiation vibrates perpendicular to the planes of the $PtCl_4^{2-}$ ions (and thus parallel to the needle (c) axis of the crystal), while the \parallel curve corresponds to the electric vector vibrating parallel to the $PtCl_4^{2-}$ planes. These reflectivities are relative values, having been taken *vs.* an aluminum mirror, and must be multiplied by approximately 0.9 to be placed on an absolute scale.

fied in part in the course of the present investigations, have shown that the identities of the species present in solutions obtained by dissolving K_2PtCl_4 and K_2PdCl_4 samples are not completely unambiguous. For instance, Chatt, Gamlen, and Orgel⁹ found that the spectra of aqueous solutions of K_2PtCl_4 changed with time. Similarly, the spectrum of K_2PdCl_4 in 1 *M* $HClO_4$ is markedly different than that found for K_2PdCl_4 in a solution containing a large excess of chloride ion.^{14,17} Further, in the course of the present studies it was found that solutions of K_2PdCl_4 in 1 *M* perchloric acid did not obey Beer's law in the 310- $m\mu$ region. The careful work on K_2PtCl_4 by Chatt and coworkers⁹ and the study of K_2PdCl_4 by Srivastava and Newman¹⁰ and Jørgensen¹¹ indicated, however, that in 2 *M* HCl solutions of K_2PdCl_4 and K_2PtCl_4 , the predominant metal-containing species are $PdCl_4^{2-}$ and $PtCl_4^{2-}$. Such solutions were here found to be quite stable spectroscopically and to possess spectra that were concentration independent over the approximate range of 10^{-2} to 10^{-5} *M*. Moreover, these spectra were consistent with crystal spectra obtained in this and previous studies.^{18,19}

In light of the above considerations, the single crystals used in this work were grown by slow evaporation of solutions prepared by dissolving K_2PtCl_4 ("purified," from Fisher Scientific Co.) or K_2PdCl_4 (K & K Laboratories) in 2 *M* HCl . The crystals were filtered free of the mother liquor when they had attained a size suitable for spectral study. Well-formed crystals with clean faces were thus obtained. Representative K_2PtCl_4 and K_2PdCl_4 crystals from such preparations were found to contain 34.11 and 43.18% Cl , respectively, compared to calculated values of 34.16 and 43.44%, and were dissolved in 2 *M* HCl to give solution spectra identical with those reported previously for the original starting materials.⁹⁻¹²

Spectral Measurements. The reflection spectra reported here were obtained using a microspectrophotometer that has been described previously.⁸ Solution studies in the far quartz ultraviolet were carried out using a Beckman DU spectrophotometer capable of being purged with nitrogen and equipped with optics

(15) A. K. Sundaram and E. B. Sandell, *J. Amer. Chem. Soc.*, **77**, 855 (1955).

(16) C. I. Sanders and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, **83**, 807 (1961).

(17) The differences between these two solutions become even more striking if the measurements are extended to somewhat higher energies than those covered by Figure 4 of ref 14.

(18) P. Day, A. F. Orchard, A. J. Thomson, and R. J. P. Williams, *J. Chem. Phys.*, **42**, 1973 (1965).

(19) D. S. Martin, Jr., and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).

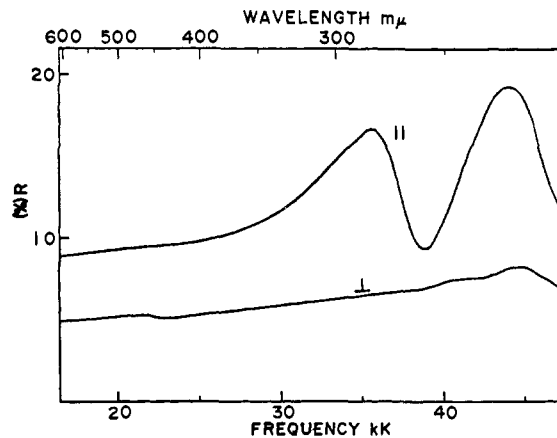


Figure 2. Polarized reflection spectra for a side face (*i.e.*, a face in the $(hk0)$ zone) of the K_2PdCl_4 single crystal. The \perp and \parallel notation has the same significance as in Figure 1, and once again relative reflectivities are reported.

that permitted measurements to a high-energy limit set by the background absorption of the aqueous chloride solutions being employed as solvents.²⁰ Other solution work entailed the use of a Perkin-Elmer 350 or a Cary 11 or 14 spectrophotometer. In all cases, the absorption due to chloride ion was canceled by using equal concentrations of this ion in the sample and reference cells.

Results and Discussion

Reflection and Solution Spectra. K_2PtCl_4 and K_2PdCl_4 form isomorphous tetragonal crystals,²¹ which are elongated along c .¹⁹ The $PtCl_4^{2-}$ and $PdCl_4^{2-}$ anions are in each case stacked, with the metal ions falling along the c axis and the anionic planes being perpendicular to it.²¹ Spectra were obtained in this work on the spectroscopically equivalent "side" faces of the crystals studied (the (100) and (010) faces, according to Dickinson²¹) with the electric vector of the incident light parallel or perpendicular to c . With the light polarized parallel to c , one observes absorption, and thus reflection, bands corresponding to those transitions that are polarized perpendicular to the plane of the anionic species, while with light polarized at right angles to the c axis, the in-plane polarizations are allowed.

Figures 1 and 2 present the reflection spectra obtained in the current study, the \perp and \parallel notation denoting respectively the curves that result when the electric vector is polarized perpendicular to and parallel with the planes of the $PtCl_4^{2-}$ and $PdCl_4^{2-}$ species. For comparison, the intense portions of the ultraviolet spectra of K_2PtCl_4 and K_2PdCl_4 in aqueous 2 *M* HCl are reported in Figures 3 and 4. The single-crystal reflection and the solution spectra reported here each represent the average of at least three independent determinations.

The presence of excess chloride ion during the determination of the curves presented in Figures 3 and 4 was necessary, as pointed out previously, to ensure the predominance of the MCl_4^{2-} type metal ions in solution, but it has the disadvantage of setting an upper limit to energies at which one may make measurements. The portions of the spectra shown in Figures 3 and 4 with dotted lines are those where, although the spectrophotometer slits were not completely open, the chloride ion interference is sufficiently great that there is reason to question the accuracy of the measurements.

(20) G. Scheibe, *Z. Phys. Chem., Abt. B*, **5**, 355 (1929).

(21) R. G. Dickinson, *J. Amer. Chem. Soc.*, **44**, 2404 (1922).

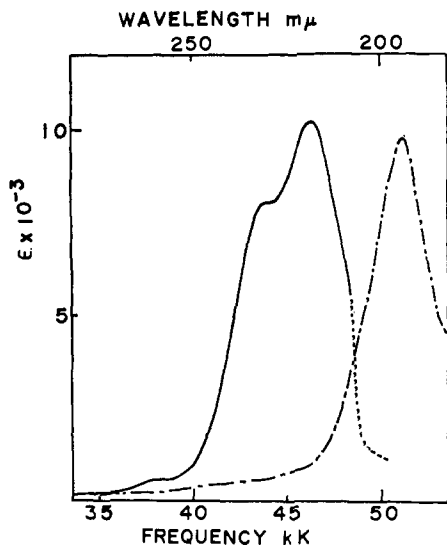


Figure 3. The spectra of K_2PtCl_4 (—) and of $Pt(NH_3)_4Cl_2$ (---) obtained in aqueous solution. In the case of K_2PtCl_4 the solution was also 2 M in HCl , and the dotted portion of the curve may thus be in doubt due to complications introduced by chloride ion absorption.

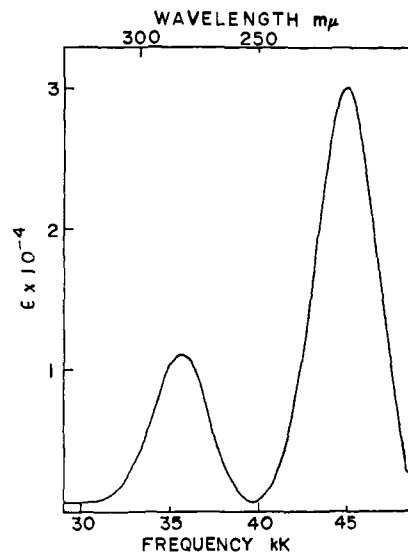


Figure 4. The spectrum of K_2PdCl_4 in aqueous solution. HCl (2 M) is also present here and thus, as in Figure 3, the dotted portion of the curve may be in doubt.

It is clear that there is a one-to-one correspondence between the major reflection peaks and the solution absorption bands apparent in Figures 1 through 4. Moreover, the reflection curves reveal that the band that peaks at 46.3 kK in the K_2PtCl_4 solution contains a major out-of-plane component, while both the $PdCl_4^{2-}$ bands are seen to be in-plane, with that which occurs at 35.7 kK in solution being completely so within the limits of the present measurements.

Just as in conventional absorption spectroscopy, one must consider the possibility that relatively minor structural features appearing in the reflection curves near the extremes of the experimentally accessible spectral region may be artifacts. Some care must thus be exercised in the interpretation of the high-energy maxima noted in the in-plane K_2PtCl_4 and the out-of-plane K_2PdCl_4 reflection spectra. The detailed discussion of this aspect of the reflection spectra will be deferred, however, until the results of the Kramers–Kronig analysis of the more strongly absorbing directions have been presented and discussed.

Kramers–Kronig Absorption Curves and Intensity Comparisons. The absorption curves that were obtained through the application of the Kramers–Kronig analysis to the K_2PtCl_4 and the K_2PdCl_4 reflection spectra are shown in Figure 5. The nature of this analysis and the details of the specific procedures followed, including those used to approximate the effects of the experimentally inaccessible reflection data, have been described in detail elsewhere.⁸ In essence, however, what is involved here is the use of the reflection data over an extended range of frequencies to compute the phase change on reflection at a given frequency. A knowledge of the phase change and reflectivity at that frequency then allows one to compute the extinction coefficient at this frequency.

The ϵ values reported in Figure 5 are based on crystal concentrations of 8.26 and 8.15 mol/l, respectively for K_2PtCl_4 and K_2PdCl_4 . It should also be noted that the extinction coefficients reported in Figure 5 are crystal ϵ 's and for comparison to solution values must be

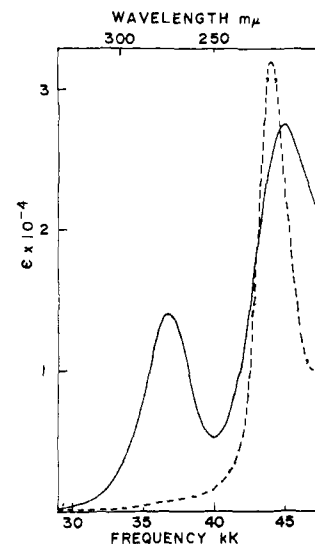


Figure 5. The absorption spectra obtained for the out-of-plane direction for K_2PtCl_4 (---) and the in-plane direction of K_2PdCl_4 (—) through Kramers–Kronig analyses of the corresponding reflection spectra of Figures 1 and 2. (The reflection data were converted to an absolute basis prior to performing the analyses.)

multiplied by $1/3$ for K_2PtCl_4 and $2/3$ for K_2PdCl_4 . (The reasoning on which these conversions are based is analogous to that presented below in the discussion of the derivation of mutually compatible transition moments from crystal and solution data.)

Table I summarizes the spectral results obtained in this work. The $|q|^2$ values (*i.e.*, the absolute values of the lengths of the transition moments squared) reported for overlapping bands represent the average of several reasonable assumptions regarding decomposition into components. Similarly, where required, several approximations were made concerning high-energy extrapolation of the bands involved and possible base line corrections. The $|q|^2$ values cited for the solution bands and the 272- $m\mu$ band of the K_2PdCl_4 crystal are felt to be those known with greatest accuracy, but the high-energy crystal transition $|q|^2$ values are thought to serve

Table I. Solution and Partial Crystal Spectral Data for K_2PtCl_4 and K_2PdCl_4

Compd	Solution data				Crystal data ^a							
	Absorption position		ϵ_{\max} , cm ⁻¹ M ⁻¹	$ q ^2$, Å ^{2b}	Reflection			Absorption				
	λ_{\max} , mμ	ν_{\max} , kK			λ_{\max} , mμ	ν_{\max} , kK	R_{\max} , % ^c	λ_{\max} , mμ	ν_{\max} , kK	ϵ_{\max} , cm ⁻¹ M ⁻¹	$ q ^2$, Å ^{2d}	Polarization
K_2PtCl_4	216 ^e	46.3 ^e	10,230 ^e	0.548 ^e	229	43.6	21.0	227	44.1	32,100 ^f	0.27	⊥ ^g
K_2PdCl_4	280	35.7	11,100	0.254	282	35.5	15.3	272	36.8	14,000 ^f	0.233	
	223	44.9	30,000	0.565	228	43.9	17.7	222	45.1	27,600 ^f	0.434	

^a Crystal data are presented here only for the "perpendicular" direction for K_2PtCl_4 and the parallel direction for K_2PdCl_4 . ^b The solution $|q|^2$ values were obtained using eq 1 with $A = 1.090 \times 10^{19}$ and, in the case of the in-plane K_2PdCl_4 transitions, dividing the results by 2. (See text.) ^c Absolute reflectivities are reported here. ^d Crystal $|q|^2$ values were obtained using eq 1 with $A = 3.270 \times 10^{19}$. ^e This band shows pronounced structure (see Figure 4) and can be divided into two roughly Gaussian bands: one at 43.7 kK (229 mμ) with $\epsilon_{\max} 7.6 \times 10^3$ and $|q|^2 = 0.260 \text{ Å}^2$ and the other at 46.9 kK (213 mμ) with $\epsilon_{\max} 8.2 \times 10^3$ and $|q|^2 = 0.288 \text{ Å}^2$. (Both $|q|^2$ values being evaluated with $A = 1.090 \times 10^{19}$ in eq 1.) ^f These are crystal ϵ and should be divided by three for the out-of-plane transition and multiplied by $2/3$ for the in-plane transitions for comparison to solution values. (See text.) ^g This band is also thought to contain an additional parallel component. (See text.)

as at least rough approximations to the intensities involved.

The $|q|^2$ values reported in Table I require additional comment, in that some care must be exercised in converting the solution and crystal values to mutually comparable bases. Simpson²² gives an expression of the following form for the computation of $|q|^2$ values from integrated intensities

$$A|q|^2 = \int \epsilon \, d \log \lambda \quad (1)$$

When this equation is derived²² with the assumption that one is dealing with a randomly oriented sample and the transition involved is between nondegenerate states, $A = 1.090 \times 10^{19}$. When either or both of these conditions is not met, however, then A must be modified appropriately or the situation otherwise recognized.

In the D_{4h} symmetry of the $PtCl_4^{2-}$ and $PdCl_4^{2-}$ ions, if one assumes that the ground state is nondegenerate, perpendicular polarization implies a nondegenerate excited state and parallel polarization a degenerate excited state. In the former case, the use of $A = 1.090 \times 10^{19}$ is appropriate in dealing with solution spectra, and thus this value has been employed to obtain the solution $|q|^2$ values reported for $PtCl_4^{2-}$ in Table I and its footnote *e*. For the in-plane polarized bands of $PdCl_4^{2-}$ the use of $A = 1.090 \times 10^{19}$ in eq 1 gives solution $|q|^2$ values that are just twice those that would be calculated using a nondegenerate ground state wave function and that for one of the degenerate pair of excited states, and thus in this case the procedure indicated in footnote *b* to Table I was followed.

In the crystal, light whose electric vector vibrates parallel to the *c* axis also has its electric vector exactly parallel to any perpendicular molecular transition moment. When the electric vector vibrates perpendicular to the crystal axis, one component of any degenerate set of transitions may be taken as having its transition moment perpendicular to the electric vector, and thus inactive, and the other as parallel to it, and therefore fully active. Consequently, the use of $A = 3.270 \times 10^{19}$ in eq 1 is appropriate for all crystal spectra reported here to obtain transition moments directly comparable to those obtained as outlined above from solution measurements.

(22) W. T. Simpson, "Theories of Electrons in Molecules," Prentice-Hall, Englewood Cliffs, N. J., 1962.

Relationship to Magnus' Green Salt (MGS) Work.

One of the original objectives of the present study was the exploration of whether or not the 46-kK solution band of K_2PtCl_4 could be the source, as had previously been suggested, of the strong out-of-plane ultraviolet band observed in the spectra of Magnus-type salts.^{2,18} The results presented here clearly demonstrate the presence of a strongly allowed transition of proper polarization in the far quartz-ultraviolet spectrum of K_2PtCl_4 and provide rather convincing support for the proposed correlation. The MGS transition is considerably more intense than the corresponding one in K_2PtCl_4 ,²³ but such changes in intensity would perhaps not be unexpected in light of the strong perturbation of the energy of the transition in going from the K_2PtCl_4 crystal to MGS (a shift of some 10 kK to the red in MGS).²

It has also been pointed out previously² that what appears to be the most consistent unified approach to the spectral perturbations noted in the MGS studies and the closely related phenomena found in the nickel glyoximates³ involves viewing the MGS transition to be $5d_{z^2} \rightarrow 6p_z$ in character. In light of the correlation of the out-of-plane K_2PtCl_4 transition with that found in MGS, the $d \rightarrow p$ assignment would be implied for K_2PtCl_4 also. Since this is contrary to the currently widely accepted assignment for this band, the assignment of the intense K_2PdCl_4 and K_2PtCl_4 transitions investigated in the present work will be considered in some detail in the section that follows.

Intense Bands. Early interpretations of the quartz-ultraviolet transitions of these systems include that by Chatt, *et al.*,⁹ of the 46 kK band in $PtCl_4^{2-}$ and those of Jørgensen^{11,12,24} concerning both $PtCl_4^{2-}$ and $PdCl_4^{2-}$. It is the assignment scheme developed by Gray and his coworkers,^{6a,25-27} however, that appears to be the most widely accepted at the present time.²⁸ Gray's

(23) Recent experiments in this laboratory (S. I. Foster and A. F. Fucaloro, unpublished work) have shown that the intensity of the MGS band is somewhat less than that previously reported but is still greater by a factor of 3 than that reported in Table I for the K_2PtCl_4 crystal transition.

(24) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962; (b) C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

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

(26) H. B. Gray, *Transition Metal Chem.*, **1**, 239 (1965).

(27) W. R. Mason, III, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 5721 (1968).

interpretation takes the 36-kK PdCl_4^{2-} solution band as being correlated with that of roughly similar intensity at 46 kK in PtCl_4^{2-} . Both bands are viewed as being composite in nature and arising from ligand-to-metal transitions ($\pi^b \rightarrow d_{x^2-y^2}$), one of which is polarized in-plane and the other out-of-plane. The 45-kK PdCl_4^{2-} band is then taken to result from a $\sigma \rightarrow d_{x^2-y^2}$ ligand-to-metal charge-transfer transition which is predicted to have in-plane polarization. The total array of allowed quartz-ultraviolet transitions occurring in these ions is thus assigned in this picture as being ligand-to-metal charge transfer in nature.

Perhaps the clearest inference to be drawn from the present study is that the strong correlation generally invoked between the 46-kK PtCl_4^{2-} band and that of PdCl_4^{2-} at 36 kK cannot be completely correct, since these two bands show such markedly different polarization characteristics. In fact, as was noted previously, in the spectral region studied here K_2PdCl_4 shows no strong out-of-plane band analogous to that found for K_2PtCl_4 . The behavior of the out-of-plane band must therefore be just the opposite to that hypothesized in the past; that is, it must shift to higher energies, rather than lower, on going from PtCl_4^{2-} to PdCl_4^{2-} . It is consequently of interest to note that the atomic $d \rightarrow p$ transitions show exactly the same behavior as one moves from Pt to Pd. If one thus uses the data given by Moore²⁹ to compute the differences in the atomic energy levels of Pd^+ that correspond to excitation from the $4d^9$ ground state to the $4d^85p^1$ excited state configurations and the comparable differences for Pt^+ , one finds the spacings for Pd^+ to be on the average some 8 kK greater than those for Pt^+ . Although spin-orbit-coupling effects render a similar direct comparison for neutral Pd and Pt less straightforward, the average energy-level differences reported by Moore corresponding to $nd^{10} \rightarrow nd^9(n+1)p^1$ ($n = 4$ for Pd and 5 for Pt) excitations differ by about 5 kK for the two metals. It is not possible to make a similar analysis for Pd^{2+} and Pt^{2+} due to the lack of the necessary data for Pt^{2+} , but it would seem reasonable to expect, on the basis of the comparison developed for the neutral and singly charged metal species,³⁰ a reasonably strong shift to higher energies in PdCl_4^{2-} compared to PtCl_4^{2-} for the suggested $nd_{z^2} \rightarrow (n+1)p_z$ transition.

As was pointed out in an earlier publication,² the extent to which the strong band found in aqueous solutions of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ at 51.2 kK corresponds to the 46-kK band of PtCl_4^{2-} provides additional support for the proposed $d_{z^2} \rightarrow p_z$ assignment, since one would expect a band analogous to the ligand-to-metal transition in PtCl_4^{2-} to shift markedly to higher energies in the ammine complex, while the $d \rightarrow p$ transition, being essentially metal \rightarrow metal, should roughly maintain its energy. The band in question is shown in Figure 3 and, except for the structure noted in the PtCl_4^{2-} band,

(28) See, for instance, ref 4 and 18 and (a) D. S. Martin, Jr., L. D. Hunter, R. Kroening, and R. F. Coley, *J. Amer. Chem. Soc.*, **93**, 5433 (1971); (b) W. Th. A. M. van der Lugt, *Chem. Phys. Lett.*, **10**, 117 (1971).

(29) C. E. Moore, *Nat. Bur. Stand. (U.S.) Circ.* **467**, Vol. III (1958).

(30) The comparisons made for the neutral and singly charged species may in fact be the most appropriate to consider here, since various theoretical treatments of PtCl_4^{2-} and PdCl_4^{2-} involving the development of self-consistent charge distributions lead to an effective charge on the central metal atom of between 0 and 1.^{6,31}

(31) L. V. Interrante and R. P. Messmer, *Inorg. Chem.*, **10**, 1174 (1971).

is seen to be very similar in appearance to it. The integrated intensity of $\text{Pt}(\text{NH}_3)_4^{2+}$ and eq 1 with $A = 1.090 \times 10^{19} \text{ \AA}^2$ lead to a $|q|^2$ value of, depending on the manner in which the high-energy portion of the band is approximated, 0.23 to 0.31 \AA^2 . This figure compares well with the value of 0.27 given in Table I for the corresponding K_2PtCl_4 crystal transition.

There appears to be little reason to doubt the assignment of the two in-plane bands of K_2PdCl_4 observed here to ligand-to-metal charge transfer, in that their polarizations and their behavior upon replacing the Cl^- ligands with other halides is as would be expected on this basis.^{24b,25} This assignment, coupled with that of the 46-kK band of PtCl_4^{2-} as a $d \rightarrow p$ transition, leads to the inference that as the charge-transfer bands shift to lower energies in K_2PdCl_4 the $d \rightarrow p$ band simultaneously shifts to higher energies. Such behavior is reasonable, since the red shift of the charge-transfer bands implies a lower potential on the metal in the palladium complex, and this relatively deeper potential well in turn suggests (in analogy, say, with the classic quantum mechanical "particle in a well" problem) a spreading apart of the metallic levels, with a resultant blue shift of transitions essentially confined to the metal.

Less Intense Bands. It will be observed in Figures 1 and 2 that the spectra for the more weakly absorbing crystal directions (the parallel K_2PtCl_4 and the perpendicular K_2PdCl_4 directions) show an increase in reflectivity as one moves from lower to higher energies and then at high energies the reflectivity begins to drop off. This behavior might be taken as indicating a relatively weak transition (but still strong enough to appear in reflection) occurring in each of these directions. As was pointed out when the reflection curves were first presented, caution should be exercised in the interpretation of the relatively weak structure seen in the high-energy portion of the experimentally available range. On the basis of the appearance of a similar in-plane structure in each of a series of Magnus-type salts involving the PtCl_4^{2-} ion,³² however, it has been concluded that the K_2PtCl_4 crystal does in fact possess an in-plane band at the approximate point indicated by the reflectivity peak shown in Figure 1. The peak seen in the out-of-plane K_2PdCl_4 spectrum, on the other hand, cannot be taken, in the absence of confirming collateral evidence, as carrying such an inference.

The structure observed in the K_2PtCl_4 46-kK solution band is consistent with the picture developed above of there actually being two electronic transitions in this region. If one further associates the higher energy solution peak with the out-of-plane single-crystal band, the data of Table I indicate that this transition has undergone a red shift in the crystal compared to solution. This is exactly the behavior that would be expected on the basis of exciton theory for a situation where the primary crystal interaction may be represented (as is the case for the out-of-plane polarization observed here) through "end-to-end" interaction of transition moments.³³ This would leave the lower energy solution component, which occurs at about 44 kK, as the in-plane band. This band shows, as is to be expected from exciton theory for "side-by-side" inter-

(32) B. G. Anex, S. I. Foster, and A. F. Fucaloro, to be submitted for publication.

(33) M. Kasha, *Radiat. Res.*, **20**, 55 (1963).

action of transition moments, an apparent blue shift on crystallization.³⁴

Table I indicates that the integrated intensity of the 46-kK solution band of K_2PtCl_4 corresponds to a total $|q|^2$ of 0.548 \AA^2 , assuming that only nondegenerate transitions are involved. If 0.27 \AA^2 of this can be associated with the perpendicular transition, 0.28 \AA^2 is associated with the degenerate band, whose $|q|^2$, according to the conventions outlined previously, would be taken as 0.14 \AA^2 . It is this value that must be compared to the 0.28 \AA^2 out-of-plane intensity when considering the relative reflectivities to be expected here. The sharply reduced effective in-plane $|q|^2$ and the apparent relative sharpness of the out-of-plane band combine to make reasonable the markedly reduced reflectivity observed in Figure 1 for the K_2PtCl_4 in-plane spectrum.

One cannot observe the low-intensity ligand-field bands of K_2PtCl_4 and K_2PdCl_4 using the room-temperature reflection techniques employed here. It will be noted, however, that the intensity of the in-plane and out-of-plane components of the ligand-field transitions are correlated with the polarizations of the low-lying allowed bands studied here in just the fashion expected on the basis of a vibronic borrowing mechanism for the acquisition of intensity by the $d \rightarrow d$ bands.² Thus, one finds that for K_2PtCl_4 the out-of-plane ligand-field components tend to be more intense than the in-plane, while for K_2PdCl_4 the opposite situation obtains.¹⁸ In other words, the relative influence of the out-of-plane transition diminishes as it retreats into the vacuum ultraviolet and the in-plane transitions move to the red, as one would expect from the resonance denominator effect thought to be operative here.

(34) The in-plane K_2PtCl_4 reflection band peaks at approximately 44.3 kK and the related absorption, as is illustrated by the data of Table I for K_2PdCl_4 , may be expected to peak somewhat to the blue of this.

Conclusion

The spectra presented here have been seen to be highly consistent with the PtCl_4^{2-} ion possessing a much lower lying 6p manifold of levels than has previously generally been thought to be the case.³⁵ At the same time, they are not inconsistent with the more conventional assignment of the ultraviolet bands of K_2PdCl_4 to ligand-to-metal charge-transfer transitions. Although the strong correlation that had been previously assumed to exist between the first allowed bands of these two systems has been shown not to be operative, evidence has been found for the existence of intensity in the 46-kK band of PtCl_4^{2-} that could, on the basis of its in-plane polarization, be correlated with the in-plane K_2PdCl_4 absorption.

Perhaps as important as the spectral information developed in this work is the demonstration it presents of the danger of using without strong collateral evidence correlations drawn from solution data in making spectral assignments. In particular, the present study demonstrates the advantages of investigating several related systems and employing the polarizations of the bands as labels to be used in following their movements as one proceeds from one compound to another.

The conclusions reached here clearly carry implications with regard to the spectra of other d^8 planar complexes. The exploration of these aspects of the spectra of selected halides and amines will be covered in subsequent papers in this series.

(35) Schatz, *et al.* (ref 13), have found in their magnetic circular dichroism (MCD) studies, however, confirmation for the assignment of the 46-kK K_2PtCl_4 band to two transitions, with the low-energy component being associated with a degenerate and the high-energy component with a nondegenerate excited state, and have supported the $d_{z^2} \rightarrow p_z$ assignment for the high-energy component. Their MCD work also provides evidence for the in-plane assignment of the 45-kK band of K_2PdCl_4 .