metal–metal bond exists and that the lowest-energy visible band is a special transition associated with the metal chain.[15] However, the case of orthorhombic nickel bis(N-methylsalicylaldiminate) [Ni(Me salim)$_2$] demonstrates the failure of this assumption. In Ni(Me salim)$_2$, the Ni atoms are lined up in exactly the same way as in Ni(DMG)$_2$, with almost identical spacing.[19] However, the single crystal spectra taken by Ferguson[20] and more recently by us (unpublished) show that the lowest-energy visible band is in-plane polarized, unlike that of Ni(DMG)$_2$. Thus, so-called "abnormal" dichroism is not a necessary companion to the nickel ion chain structure found in Ni(DMG)$_2$. Also, inspection of the single-crystal spectra of Ni(DMG)$_2$ shows that the out-of-plane dichroism is really very slight, being caused merely by a slightly broader red tail of the visible absorption in the out-of-plane direction. Therefore, the *apparent* striking dichroism is not much more than a consequence of the fact that the eye is responding only to light in the fre-

quency region of the red tail, as the absorption of light by the crystal is practically total in the regions of the shoulder or maximum. Finally, there is nothing abnormal in out-of-plane band polarization for a planar molecule. The "abnormal" designation arises from the fact that π–π transitions of planar organic molecules are, to a good approximation, symmetry forbidden in out-of-plane polarization. However, when other types of transitions can occur (particularly where a transition metal ion is involved) many will be out-of-plane permitted.

The temperature effect on the single-crystal absorption spectrum of Ni(DMG)$_2$ (Fig. 3) is very small. This fact hints at one of two alternatives: (1) the transition probability is not caused by the vibronic mechanism and (2) the transition probability is produced by vibronic coupling to very high-frequency modes. One cannot yet choose between these alternatives. There is a small red shift as the temperature is decreased; it is evident both in the single crystal (Fig. 3) and in polycrystalline samples.[1] We presume that this shift is caused by sample contraction and is merely another manifestation of the red pressure shift.[4]

(19) E. C. Lingafelter, G. L. Simmons, B. B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, **19**, 1222 (1961).
(20) J. Ferguson, *J. Chem. Phys.*, **34**, 611 (1961).

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Vibronic Absorption Spectrum and Dichroism of Potassium Tetrachloroplatinate(II)[1]

BY DON S. MARTIN, JR., AND CHARLES A. LENHARDT

The absorption spectrum from 550 to 270 mμ for a single crystal of K$_2$PtCl$_4$, with light polarized parallel and normal to the symmetry axis of the PtCl$_4{}^{-2}$ ion, is reported. Absorption peaks are well resolved so that a shift in maxima between alternative polarizations is apparent. A consideration of the vibronic interactions permits the assignment of the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. An assignment of other transitions is proposed on the basis of the shift of maxima which orders the d-orbitals $d_{z^2} > d_{xy} > d_{xz,yz}$. The influence of Jahn–Teller splitting of the excited E$_g$ state is discussed.

Introduction

The absorption spectrum of the square-planar ion, PtCl$_4{}^{-2}$, in aqueous solution contains four peaks which can be attributed to transitions between d-electron states. However, various authors have proposed different transition assignments for these observed peaks.[2-4]

The spectrum of a freshly prepared K$_2$PtCl$_4$ solution in dilute HCl is shown in Fig. 1. The intense absorption above 36,000 cm.$^{-1}$ is presumably due to a charge-transfer process.[4] Below 36,000 cm.$^{-1}$, two strong peaks, labeled 3 and 4, and a weaker peak, 2, are clearly evident. The $\bar{\nu}_{max}$, ϵ_{max}, and oscillator strengths

from a Gaussian analysis for the spectrum are in Table I. As a consequence of the Gaussian analysis a very weak absorption (1), of perhaps questionable existence, appears at about 17,000 cm.$^{-1}$. As shown in Fig. 1, the sum of the Gaussian components deviates by a similar amount in the region of 23,000 cm.$^{-1}$.

Crystals of K$_2$PtCl$_4$ are ideally suited for the study of polarized spectra for this ion since each PtCl$_4{}^{-2}$ occupies a site in the unit cell with the full D$_{4h}$ symmetry and with one ion per unit cell.[5] Therefore the fourfold symmetry axis (z-axis) is aligned with the crystallographic c-axis. The ions lie directly over one another with an eclipsed arrangement of chlorides and with platinum atoms separated along the z-axis by 4.13 Å. With the inversion symmetry and the exact alignment of the symmetry axes in the crystals, their polarized

(1) Contribution No. 1452. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
(2) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).
(3) R. F. Fenske, D. S. Martin, Jr., and K. Ruedenberg, *Inorg. Chem.*, **1**, 441 (1962).
(4) H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).
(5) R. G. Dickinson, *ibid.*, **44**, 2404 (1922).

TABLE I

ABSORPTION PEAKS IN THE SPECTRUM OF AQUEOUS PtCl$_4^{-2}$

Peak	ν_{max}, cm.$^{-1}$	Extinction coeff., ϵ_{max}	Oscillator strength $\times$ 10^4	Ref. 2	Ref. 3	Ref. 4	Present work
						Assignment excited state	
1	17,200	(2)	(0.3)	^{3}A$_{2g}$		^{3}A$_{2g}$	
2	21,000	15	2.8	^{3}E$_g$	(^{3}A$_{2g}$, ^{3}B$_{1g}$)	^{1}A$_{2g}$	^{1}B$_{1g}$
3	25,400	57	7.3	^{1}A$_{2g}$	^{1}A$_{2g}$	^{1}B$_{1g}$	^{1}A$_{2g}$
4	30,300	62	12.	^{1}E$_g$	^{1}B$_{1g}$	^{1}E$_g$	^{1}E$_g$

spectra provide a rigorous test for the theory which attributes the intensity of transitions among the d-states to the mixing of odd states by vibronic interactions of asymmetric vibrations.

Yamada[6] observed the polarized absorption spectra of single crystals by a procedure in which light passed through a microcrystal on a microscope stage with a sectorphotometer and photographic recording. These spectra with limited resolution indicated a weak unpolarized absorption in the vicinity of 20,000 cm.$^{-1}$, absorption polarized more strongly in the plane of the ions (x–y) from *ca.* 21,000 to 29,000 cm.$^{-1}$, and absorption polarized more strongly normal to the plane of the ions (z) beyond 29,000 cm.$^{-1}$. Resolution was sufficiently poor that correlation of the absorption in the crystals with the solution peaks was somewhat questionable.

A Pt^{+2} ion has a 5d^8 electronic configuration, and ambiguity in the assignment of the electronic transitions in PtCl$_4^{-2}$ arises from the uncertainty in the extent of the tetragonal distortion imposed on the octahedral splitting of the d-orbitals in the square-planar ions. Possible arrangements of the orbital splitting are shown in Fig. 2. Since the ions are diamagnetic, the ground state is considered to be ^{1}A$_{1g}$ with the d$_{x^2-y^2}$-orbital unoccupied. The three lowest energy singlet–singlet transitions may be considered one-electron transfers from the other d-orbitals to the d$_{x^2-y^2}$-orbital. In a molecular orbital description the unoccupied orbital is strongly antibonding. These transitions may be designated d$_{z^2} \rightarrow$ d$_{x^2-y^2}$, ^{1}A$_{1g} \rightarrow$ ^{1}B$_{1g}$; d$_{xy} \rightarrow$ d$_{x^2-y^2}$, ^{1}A$_{1g} \rightarrow$ ^{1}A$_{2g}$; d$_{xz,yz} \rightarrow$ d$_{x^2-y^2}$, ^{1}A$_{1g} \rightarrow$ ^{1}E$_g$. In addition, singlet–triplet transitions must be considered a possibility in view of the relatively large spin–orbit coupling in platinum. Since the ground and excited states are both even, the electronic transitions are forbidden by symmetry but presumably occur by a vibronic mechanism involving asymmetric vibrations. The transition assignments proposed by previous authors are included in Table I. In addition, Perumareddi, Liehr, and Adamson[7] have reported that their consideration of square-planar cyanide complexes indicated the d$_{z^2}$ orbital lies above the d$_{xy}$.

The present work describes the polarized absorption spectra of a single crystal of K$_2$PtCl$_4$ with sufficient resolution to offer considerable inferences regarding the electronic transition assignments.

Experimental

The K$_2$PtCl$_4$ was prepared by the oxalate reduction of K$_2$PtCl$_6$ as has been described in earlier work.[8] Several repeated crystal-
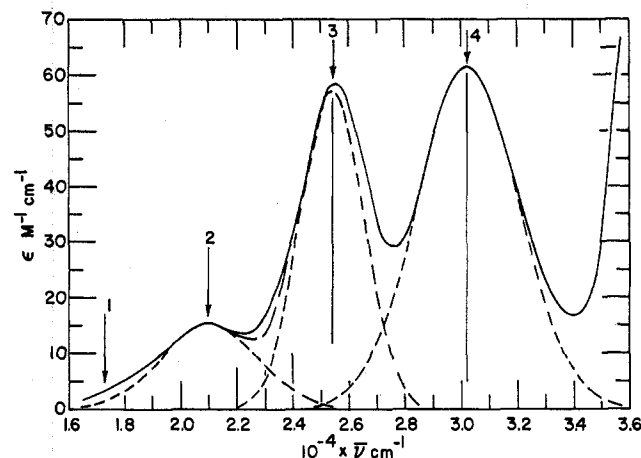
Fig. 1.—Absorption spectrum of freshly prepared aqueous solution of K$_2$PtCl$_4$; 0.0150 *M* K$_2$PtCl$_4$, 0.32 *M* HCl: ———, observed spectrum; — — — —, Gaussian components; — —, sum of Gaussian components.

lizations from dilute HCl by evaporation at room temperature were performed to effect separation of the platinum complex salt from KCl. The K$_2$PtCl$_4$ normally crystallizes as needles with the *c*-axis along the long dimension. However, from among several grams of crystals were found two single-crystal plates thin enough for spectrophotometric work. Both crystals gave comparable results, and the spectra which have been reproduced in Fig. 3 were obtained with a 0.32-mg. crystal of about 2-mm.^{2} area, so the average thickness was about 50 μ. These crystals had the *c*-axis in the face. A microscopic examination showed some grooves in the faces. These striations were oriented in the *c*-direction. With the small size and fragility of the crystals, polishing was infeasible.

The crystals were cemented over a pinhole in a 5-mil copper sheet by a drop of thinned lacquer at each end. The copper sheet bearing the crystal was mounted in the beam of a Cary Model 14 spectrophotometer at the slit image in the sample compartment. The beam in the reference compartment was then "stopped down" by an orifice defined by opaque tape on a silica plate. The orifice size was adjusted until a recording over a spectral region to be studied could be obtained with the slits operative. Generally, a larger orifice and slit opening of less than 0.5 mm. could be used at wave lengths above 420 mμ. Spectra in the ultraviolet were obtained with slits of less than 2 mm. It was possible to relate the curves with different orifices by recording a region with both the orifices. Beam convergence at the crystal was less than 9°.

The light beam in the spectrophotometer sample compartment was polarized by a Glan calcite prism polarizer. Optical densities were recorded with this polarizer alone set in the two orientations utilized with the crystal. The optical density of the polarizer was then subtracted from that observed with the crystal at each wave length. The optical density of the polarizer varied gradually from 0.76 at 550 mμ to 1.3 at 270 mμ. The optical density in the two orientations differed by less than 0.05 at all wave lengths in this region.

Two spectra, obtained for light polarized with the electric

(6) S. Yamada, *J. Am. Chem. Soc.*, **73**, 1182 (1951).

(7) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *ibid.*, **85**, 249 (1963).

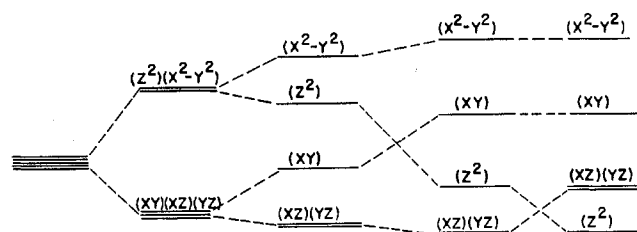(8) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961).

Fig. 2.—Possible arrangement of d-orbitals in a complex with D_{4h} symmetry. Degeneracies under the octahedral splitting are further broken as a tetragonal distortion, increasing toward the right, is applied.
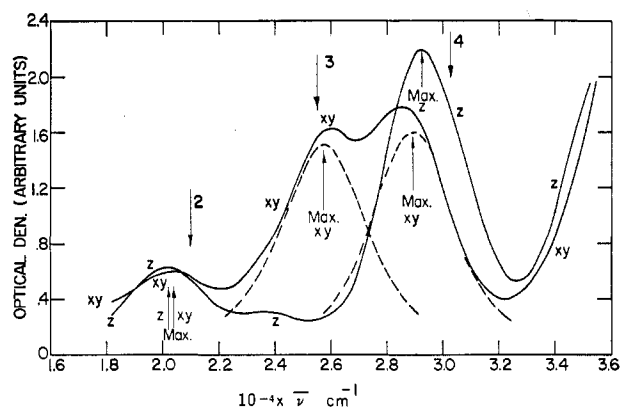

Fig. 3.—Absorption spectrum of K_2PtCl_4 crystal in polarized light. The optical density is in arbitrary units. Dashed lines indicate the Gaussian components for the x–y polarization.

vector along the c-axis, i.e., "z polarization" for the planar ion, and normal to the c-axis, "x–y polarization," have been presented in Fig. 3. These spectra are given as typical of many which have been recorded with different arrangements including reversal of crystal orientation and with the polarizer mounted either before or after the crystal. As might be expected, where different portions of the photomultiplier surface receive the light, relative heights of the two spectra were somewhat variable. Thus, although the peak at 29,200 cm.$^{-1}$ in z polarization was generally higher than the peak at 28,900 cm.$^{-1}$ in x–y polarization, no absolute claim about these intensities is possible since the heights in different curves were somewhat variable. The relative peak heights of any one curve did, however, appear to be reproducible. Also, the relative locations of maxima between the two curves were consistently reproduced to within ca. ± 1 mμ. The apparent double peak in the spectrum for x–y polarization was satisfactorily resolved as Gaussian components, which are shown as dashed lines in Fig. 3. The energies corresponding to the peaks in the spectra are included in Table II.

TABLE II

ENERGIES FOR THE ABSORPTION PEAKS IN THE POLARIZED
SPECTRUM OF K_2PtCl_4 CRYSTALS

Polarization		Transition
z	xy	assignment
Energy, cm.$^{-1}$		
20,200	20,400	$^1A_{1g} \rightarrow {}^1B_{1g}$
	25,700^a	$^1A_{1g} \rightarrow {}^1A_{2g}$
29,200	28,900^a	$^1A_{1g} \rightarrow {}^1E_g$

^{a} For components resolved by Gaussian analysis.

Results and Discussion

The d–d electronic transitions by a dipole process are forbidden under a tetragonal symmetry. However, they can occur by vibronic interactions as asymmetric vibrations mix in asymmetric wave functions. If in-
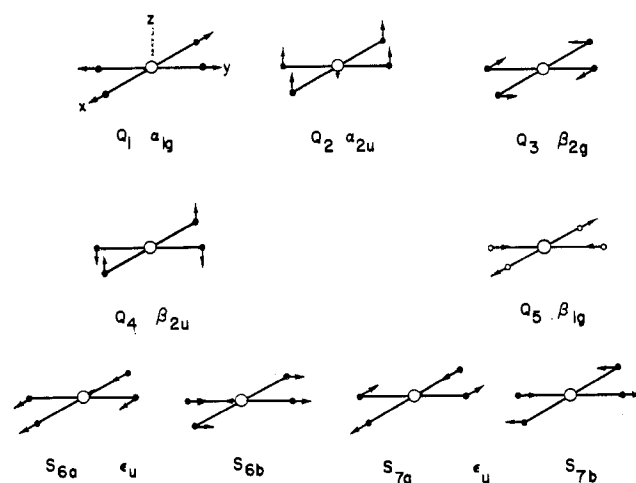

Fig. 4.—Symmetry coordinates for the vibrations of a $PtCl_4^{-2}$ ion.

teractions with other ions in the crystals are neglected and if Q_i designates an asymmetric normal vibration coordinate, then, according to first-order perturbation theory, the expression for the wave function can be written[9]

$$\psi = \psi_g - \sum_i \sum_{\psi_u} Q_i c \psi_u \qquad (1)$$

where ψ_g is the unperturbed wave function, ψ_u is an asymmetric wave function, and

$$c = \int \psi_g^* \frac{\partial H}{\partial Q_i} \psi_u \, d\tau / (E_u - E_g)$$

The product $Q_i \psi_u$ in each term is required to have the symmetry of ψ_g. In accordance with the Born and Oppenheimer approximation the total wave function Ψ is written as the product

$$\Psi = \psi_{elect} \chi \qquad (2)$$

where $\chi(Q_i, Q_j \ldots)$ is the vibrational wave function for the nuclei. The transition moment for a dipole process from state 1 to state 2 becomes

$$\int \Psi_1^* r \Psi_2 \, d\tau = \sum_i \int \sum_{\psi_u} [(c_1 \psi_u)^* r \psi_{2g} +$$
$$\psi_{1g} r^* (c_2 \psi_u)] \, d\tau_{elect} \int \chi_1 Q_i \chi_2 \, d\tau_{vib} \qquad (3)$$

The transition moment will therefore contain nonzero terms, and low intensities are permitted for the "symmetry-forbidden" transitions.

In case the product $\psi_1 \psi_2 Q_i$ contains a basis function for the representation, a_{2u}, which characterizes z, polarization with the electric vector in the z-direction will occur as a consequence of this vibration. If the product $\psi_1 \psi_2 Q_i$ contains the basis function for the e_u representation, which characterizes x,y, polarization in the plane of the ions will occur.

A set of symmetry coordinates for the vibrations of a square-planar $PtCl_4^{-2}$ ion are shown in Fig. 4. Vibrational frequencies for the electronic ground state which are available from recent infrared and Raman studies

(9) (a) W. Moffitt and C. J. Ballhausen, *Ann. Rev. Phys. Chem.*, **7**, 107 (1956); (b) C. J. Ballhausen, *Progr. Inorg. Chem.*, **2**, 251 (1960); (c) A. D. Liehr, *Advan. Chem. Phys.*, **5**, 241 (1963).

are included in Table III. The nondegenerate vibrations, designated by the Q_i's, are normal vibrations. There are, in addition, two sets of e_u vibrations designated by the symmetry coordinates, $S_{6a,b}$, $S_{7a,b}$. The normal vibrations will be linear combinations of the a pairs and the b pairs of these symmetry coordinates. Wilson[10] has given an analysis of the vibrations by a simple valence bond force method and Maccoll[11] has used a more general potential function. With a heavy central atom and with stretching force constants much larger than those for bending, the normal coordinates for vibrations 6 and 7 will be one degenerate pair which is largely a stretching motion and one pair which is primarily an in-plane bending motion. It is to be noted that the stretching frequencies, ranging from 304 to 335 cm.$^{-1}$, are, as expected, considerably greater than the bending frequency of 164 cm.$^{-1}$ for Q_3. Further, the out-of-plane bending frequencies for Q_2 and Q_4 are expected to be still lower than Q_3.

TABLE III

VIBRATIONS FOR THE PtCl₄$^{-2}$ ION WITH D$_{4h}$ SYMMETRY

Vibration[a]	Symmetry representation	ν, cm.$^{-1}$	Determination
Q_1	α_{1g}	335	Raman[b]
Q_2	α_{2u}		
Q_3	β_{2g}	164	Raman[b]
Q_4	β_{2u}		
Q_5	β_{1g}	304	Raman[b]
$S_{6a,b}$	ϵ_u	328	Infrared[c] (primarily stretching)
$S_{7a,b}$	ϵ_u		

[a] The enumeration of the vibrations is that of A. Maccoll, J. Proc. Roy. Soc. N.S. Wales, **77**, 130 (1944). However, the designation of the symmetry representation is in accord with the location of the x and y axes as shown in Fig. 4 and the currently accepted character table for D$_{4h}$ symmetry [H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1944, pp. 386 and 387; F. A. Cotton, "Chemical Applications of Group Theory," John Wiley and Sons, New York, N. Y., 1963, Appendix II. [b] H. Stammreich and R. Forneris, Spectrochim. Acta, **16**, 363 (1960). [c] D. M. Adams, Proc. Chem. Soc., 335 (1961).

The spectrum of the PtCl₄$^{-2}$ ion involves the broad bands which are typical of coordination complexes. The broadness of the bands is due to the presence of symmetric vibration progressions.[12] Thus, as is shown in Fig. 5a for nondegenerate states, the equilibrium position with respect to the Q_1 (α_{1g}) stretching vibration does not coincide with that for the ground state. It is therefore expected from the Franck-Condon principle that the electronic excitation will lead most probably to a highly excited Q_1 vibrational level with a distribution of vibrational states about this most probable one. Of course, additional broadening will occur as higher vibrational states of the electronic ground state are thermally excited. The form of the transition moment, eq. 3, indicates that for the exciting asymmetric vibra-

(10) E. B. Wilson, Jr., J. Chem. Phys., **3**, 59 (1935).
(11) A. Maccoll, J. Proc. Roy. Soc. N.S. Wales, **77**, 130 (1944).
(12) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 188.
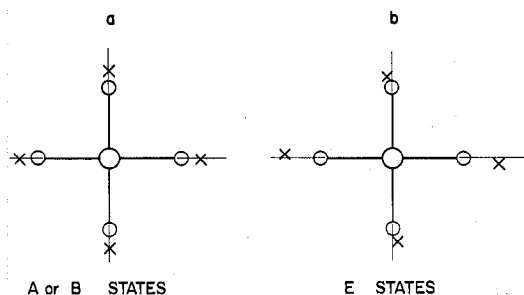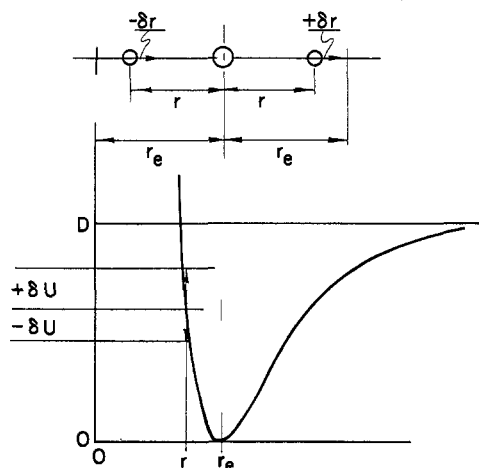

Fig. 5.—Expected equilibrium nuclear positions for the excited states; a, A or B states; b, E states in which Jahn-Teller distortion for the Q_3 and Q_5 coordinates may occur: O, ground state positions; X, excited state positions.

tion, Q_i, the most probable transition will involve a change of the vibration quantum number, Δn_i, by ± 1. This will be similar to the selection rule for simple vibrational transitions. Some failure of this selection rule, which may occur because the force constant of the excited state differs from that of the ground state, is not expected to be serious. Therefore, if the complex is at low temperatures so the Q_i vibration is in its ground state for the majority of ions, the transition will be primarily to the first excited state and an energy $\bar{\nu}_i$ will be added to the transition energy. As higher vibrational states are thermally excited, and transitions with $\Delta n_i = -1$ can occur, the location of the peak will shift to lower energies. Therefore a transition which is excited by a stretching vibration, which must have ϵ_u symmetry for PtCl₄$^{-2}$, should be displaced to slightly higher energies from one excited only by bending vibrations, and this separation should be reduced as the temperature increases. This feature may account for the observation that the same electronic transition has its maxima at slightly different energies in the opposite polarizations. If such is indeed the case then the peaks in Fig. 3 can be identified in the following way.

The polarizations required from the symmetry for each of the three singlet → singlet transitions excited by the various asymmetric vibrations are listed in Table IV. The peak at 25,700 cm.$^{-1}$ occurs only in x-y polarization and therefore is clearly indicated to be the $d_{xy} \rightarrow d_{x^2-y^2}$, $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. The peak at 20,200 cm.$^{-1}$ in z polarization is shifted to 20,400 cm.$^{-1}$ in x-y polarization. This is just the magnitude of shift, within the accuracy of the measurements, to be expected if the x-y-polarization was excited primarily by the ϵ_u stretching vibration and the z by the out-of-plane bending vibrations required for the transition $d_{z^2} \rightarrow d_{x^2-y^2}$, $^1A_{1g} \rightarrow {}^1B_{1g}$. The intensity is apparently comparable for the x-y and the z polarizations.

TABLE IV

POLARIZATION INDICATED FOR THE SINGLET-SINGLET DIPOLE TRANSITIONS IN PtCl₄$^{-2}$: d^8 WITH D$_{4h}$ SYMMETRY

		Transition		
Vibration		$^1A_{1g} \rightarrow {}^1B_{1g}$ ($d_{z^2} \rightarrow d_{x^2-y^2}$)	$^1A_{1g} \rightarrow {}^1A_{2g}$ ($d_{xy} \rightarrow d_{x^2-y^2}$)	$^1A_{1g} \rightarrow {}^1E$ ($d_{xz,yz} \rightarrow d_{x^2-y^2}$)
S_6, S_7	ϵ_u	x,y	x,y	z
Q_2	α_{2u}	...	...	x,y
Q_4	β_{2u}	z	...	x,y

Fig. 6.—Morse potential function for bond stretching utilized for evaluating an asymmetrical stretching force constant.

The peak at 28,900 cm.$^{-1}$ in x–y polarization falls at 29,200 cm.$^{-1}$ in z polarization. The greater energy in z polarization would be consistent with the transition $d_{xz,yz} \rightarrow d_{x^2-y^2}$, $^1A_{1g} \rightarrow {}^1E_g$. However the magnitude of the shift, 300 cm.$^{-1}$, is sufficiently great to deserve special consideration. The actual separation in the observed maxima in the spectra was 700 cm.$^{-1}$, but the peak in x–y polarization was obviously shifted by the presence of the adjacent transition at 25,700 cm.$^{-1}$, as indicated in Fig. 3.

It does not seem that the separation between the peaks can be substantially less than the 300 cm.$^{-1}$ as indicated in this figure and in Table II. The E_g state is subject to Jahn–Teller distortions, with respect to the Q_3 (β_{2g} in-plane bending) and the Q_5 (β_{1g} stretching) vibrations.[13] The Frank–Condon principle requires that the electronic transition carry the ion into the same nuclear configuration as the ground state. However, the possible equilibrium positions for nuclei will be as shown in Fig. 5b. A Jahn–Teller distortion can result in an extraordinarily high stretch for two of the opposing bonds. An ϵ_u stretching vibration corresponds to an increase and a decrease of the opposite bonds. Therefore since the bonds are shorter than the equilibrium values an anharmonicity in the potential function for the bond stretching will effectively increase the force constant for the ϵ_u stretching vibration. To estimate the possible influence of the anharmonicity, the simple system in Fig. 6 was considered. A Morse function

$$U = D[1 - e^{-a(r-r_e)}]^2 \qquad (4)$$

was taken as the potential function for the bond stretching where r_e is the equilibrium bond length. The two bonds were considered to be compressed equally to $r < r_e$. The expression for the change in potential energy, δU, for the changes $+ \delta r$ and $- \delta r$, corresponding to the asymmetric stretch, was written as a power series in δr. This expression through the cubic terms in δr is

$$\delta U = D[-4e^{-a(r-r_e)} + 8e^{-2a(r-r_e)}]a^2\delta r^2/2! \qquad (5)$$

The force constant for the asymmetric stretch is there-

(13) A. D. Liehr, *Progr. Inorg. Chem.*, **4**, 455 (1962).

fore $4Da^2$ for $r = r_e$ and $U = 0$. For $U = {}^1/_4D$, $r < r_e$, it is $12Da^2$ or three times the force constant at the equilibrium positions. Since $\bar{\nu}_4$ is proportional to $k_i^{1/2}$ the anharmonicity for this distortion has increased $\bar{\nu}$ by the factor $\sqrt{3}$ by this excitation of the symmetric stretch.

The observed differences in the peaks for the $^1A_{1g} \rightarrow {}^1E_g$ transition therefore appear feasible, but they do indicate rather violent distortions in the excited state. It is accordingly proposed that the excited state suffers a considerable Jahn–Teller distortion. However, since the nuclear configuration of the ground state is retained, and the potential functions for the two Jahn–Teller states coincide for D_{4h} symmetry, no Jahn–Teller splitting of the state is observed.

The proposed assignment of levels has been included in Table II. Such an assignment requires that $d_{z^2} > d_{xy} > d_{xz,yz}$ which is just the ordering Perumareddi, Liehr, and Adamson[7] indicated was required by their analysis of cyanide spectra. The point-dipole model for crystal-field energies, which was treated by Fenske, Martin, and Ruedenberg,[3] appears not to give a satisfactory description for the levels. Thus in their plot of energy levels *vs.* the dipole moment parameter the $^1B_{1g}$ state did not fall below $^1A_{2g}$ until the moment was so small that the ground state became a triplet. In a molecular orbital description the $d_{x^2-y^2}$ orbital becomes a strongly antibonding orbital, and the d_{z^2} orbital also contains some antibonding character from its interaction in the formation of the a_{1g} bonding orbital. As a consequence of these features the splitting corresponds to a weak tetragonal distortion of an octahedral configuration. Obviously, the distortion is great enough to bring the $^1A_{1g}$ below all the triplet states.

It appears that there is a satisfactory correspondence of crystal peaks to peaks 2, 3, and 4 for the solution. Peak 2 is shifted 700 cm.$^{-1}$ and peak 4 1300 cm.$^{-1}$ to higher energy on the average for solution. However, peak 3 has been shifted less, to 300 cm.$^{-1}$ lower energy in solution. The greater width of peak 4 over peak 3 reflects the splitting of the two polarized components. The oscillator strengths were calculated for the Gaussian components of Fig. 3 from the half-widths and the estimated molar extinction coefficients. The oscillator strength for each transition was then calculated by eq. 6 to take account of the random orientation of the ions with respect to the light beam.

$$f_{soln} = {}^2/_3 f_{xy} + {}^1/_3 f_z \qquad (6)$$

These calculated oscillator strengths were all one-half the values for the corresponding solution peaks. However, the area of the irregularly shaped crystal and therefore its thickness was only approximately evaluated. The assignment of the transitions given in Table I is therefore proposed on the basis of the correspondence between the peaks and the foregoing considerations.

In solution it is likely that solvent molecules bond weakly as labile ligands, at the axial positions. Such a

configuration corresponds to a tetragonally distorted octahedron. The d_{xy} and $d_{x^2-y^2}$ orbitals are expected to experience equal energy changes by such distortion, and it is noted that the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition (peak 3) is nearly at the same frequency in both the crystal and the solution. It is somewhat surprising that the tetragonal distortion from the octahedral is greater in aqueous solution, where the Pt(II) is expected to be bonded to axial H_2O ligands, than in the crystal. The feature that the anions are packed one directly over another along the symmetry axes of the crystal apparently causes the decrease in tetragonal distortion in the crystal.

The oscillator strength for peak 2 is about 0.4 to 0.2 that of those for peaks 3 and 4, respectively, which are doubtless singlet–singlet transitions. It appears therefore more satisfactory to attribute peak 2 and the corresponding peaks in the crystal spectra to a singlet–singlet transition. The singlet–triplet transitions, one of

which may correspond to the barely discernible peak 1, are then at least an order of magnitude weaker.

It may be possible that the temperature dependence of the spectrum will offer a means to test the proposals in this paper. As thermal excitation of vibrations in the ground state are reduced, a band excited exclusively by the stretching modes should show a lower temperature dependence of intensity than one excited by the bending vibration. Bands should be sharpened and the differences between peaks in the z and the x–y polarization should increase somewhat. Plans are underway to attempt the measurement of these spectra down to liquid nitrogen temperatures.

Substitution Reactions of Trichloroammineplatinate(II) Ion and the *trans* Effect[1a,b]

BY MARY ANN TUCKER, CLIFFORD B. COLVIN, AND DON S. MARTIN, JR.

The acid and base hydrolyses for trichloroammineplatinate(II) ion have been followed spectrophotometrically. Both reactions are reversible in high chloride at pH <4. The six rate constants characterizing the three reactions at 20 and 25° have been evaluated.

$$[Pt(NH_3)Cl_3]^- + H_2O \xrightleftharpoons{} cis\text{-}[Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$[Pt(NH_3)Cl_3]^- + H_2O \xrightleftharpoons{} trans\text{-}[Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$cis\text{-}[Pt(NH_3)Cl_2(H_2O)] \xrightleftharpoons{} trans\text{-}[Pt(NH_3)Cl_2(H_2O)]$$
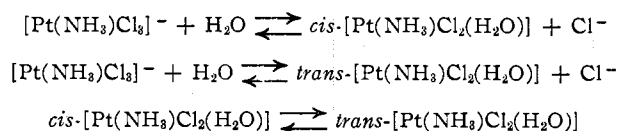
The last reaction is considered to occur *via* the acid hydrolysis of each isomer to $cis\text{-}[Pt(NH_3)Cl(H_2O)_2]^+$. The assigned rate constants account for chloride-exchange rates. The significance of the results to the quantitative expression of the *trans* and *cis* effects is discussed.

Introduction

An extensive spectrophotometric study of the kinetics of the reversible acid and base hydrolysis reactions of the $[Pt(NH_3)Cl_3]^-$ ion has been completed. It has now been possible to evaluate individual reactivities for sterically different chloride ligands. Accordingly, the conclusions of Elleman, Reishus, and Martin,[2a,b] based on chemical and chloride isotopic exchange kinetics, have been revised and extended.

As a square-planar complex of platinum(II), [Pt-

$(NH_3)Cl_3]^-$ has two chemically different types of chloride ligands. The two chlorides, designated the "*cis*-chlorides," *cis* to the NH_3 are equivalent from symmetry. The "*trans*-chloride" is the single ligand *trans* to NH_3. A complete reaction scheme for all the possibilities of the successive double aquation (acid hydrolysis) is shown in Fig. 1 together with the designation of the pertinent rate constants and equilibrium quotients.

Since a large number of concentration variables must be considered, the symbols below have been selected to provide convenience in recognition and typographical economy. All the variables indicated are concentrations in moles/l. (*M*). A subscript 0 designates a condition at the initial time, a subscript ∞ designates an equilibrium condition, and a sub-

(1) (a) Contribution No. 1489. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) presented to the Inorganic Division, 145th National Meeting of the American Chemical Society, Sept. 12, 1963.

(2) (a) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**. 536 (1958); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).