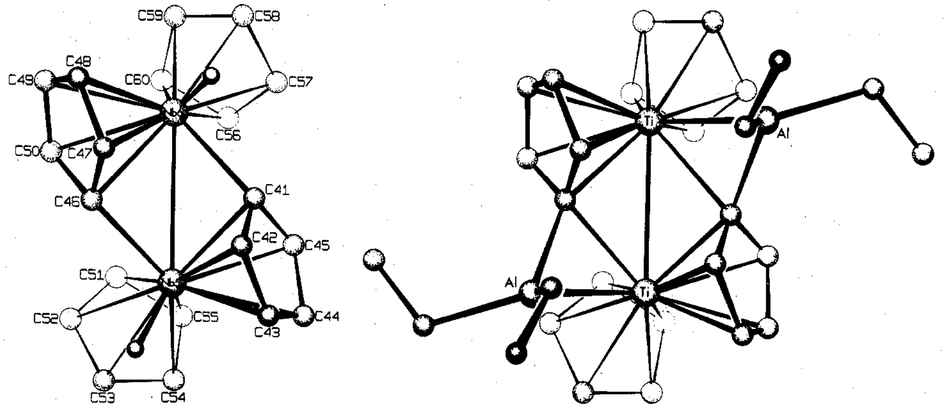

Figure 4. A comparison of the molecular structure of $[(C_5H_5)(C_5H_4)NbH]_2$ and $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$. The coordinates for the latter structure were taken from ref 4.

for one other ligand, ψ_2 and ψ_3 are used for two other ligands, and ψ_1, ψ_2, and ψ_3 are used for three other ligands. Other observed structures which can be generally rationalized in terms of the structure in Figure 3 are listed in Table VIII. Table VIII also lists the dihedral angles found between the cyclopentadienyl rings. The spread of nearly a factor of 2 in the dihedral angles illustrates the flexibility in this type of structure (Figure 3). Presumably other complexes, with as yet unknown structures, such as $(C_5H_5)_2NbH_3$, $(C_5H_5)_2Nb(H)PEt_3$, and $(C_5H_5)_2Nb(H)C_2H_4$[5] are also based on this type of structure.

The bridging geometry in $(C_5H_5)(CO)Mo(C_5H_4)Mn(CO)_4$ is similar to that found here for $[(C_5H_5)(C_5H_4)NbH]_2$; the shorter Mo-Mn distance (2.961 Å) results perhaps from the less rigid constraints of a single bridging C_5H_4 ligand. A comparison with the $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ structure[4] is particularly interesting. The latter structure was reported to contain bridging C_5H_5 ligands in addition to terminal C_5H_5 ligands. A comparison with $[(C_5H_5)(C_5H_4)NbH]_2$ is shown in Figure 4. These accurately drawn coordinates show that the bridging geometries are the same for the two structures; the titanium structure must also contain bridging C_5H_4 ligands. Wailes and Weigold came to the same conclusion from chemical evidence.[26] The hydride hydrogen in the niobocene dimer is replaced by a bridging $(C_2H_5)_2Al$ in the $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ structure.

We suggested the possibility of bridging C_5H_4 ligands for the titanocene dimer, $[(C_5H_5)(C_5H_4)TiH]_2$,[27] based on the similarities shown in Figure 4. Brintzinger and Bercaw[27] proposed bridging hydrogens for $[(C_5H_5)(C_5H_4)TiH]_2$ with terminal σ-bonded C_5H_4 ligands. Clearly a structure determination is needed on the titanocene dimer to establish the nature of the bridging structure.

Registry No. $[(C_5H_5)(C_5H_4)NbH]_2$, 11-105-934.

(26) P. C. Wailes and H. Weigold, *J. Organometal. Chem.*, 24, 713 (1970).

(27) H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 92, 6182 (1970).

Contribution from the Ames Laboratory, U. S. Atomic Energy Commission,
and the Chemistry Department, Iowa State University, Ames, Iowa 50010

Crystal Optics and Polarized Absorption Spectra for Tetraammineplatinum(II) Tetrachloroplatinate(II), Magnus' Green Salt

DON S. MARTIN, Jr.,* RHONDA M. RUSH, ROY F. KROENING, and PHILLIP E. FANWICK

Received June 29, 1972

The absorption spectra of small crystals of Magnus' green salt have been recorded at 300 and 15°K for light polarized in the directions of the *a* and *c* axes of the tetragonal crystals. In *a* polarization, a band at 25,000 cm^{-1} appears to be vibronically excited from the temperature dependence of its intensity. For *c* polarization, a band at *ca.* 16,500 cm^{-1} is also vibronically excited. There is no maximum in *c* polarization at 25,000 cm. Small crystals, about 10 μ thick and 10^{-2} mm^2 in cross section, had surfaces of sufficient optical quality that interference was observed in regions of low absorption for both polarizations. The indices of refraction could be determined by the shift in interference minima for crystals which were rotated in the beam. Values of the refractive indices are $n_a = 1.90 \pm 0.02$ and $n_c = 2.32 \pm 0.03$.

Introduction

Crystals of $[Pt(NH_3)_4][PtCl_4]$, Magnus' green salt (MGS), have a deep green color. Their color has attracted attention because many crystals and aqueous solutions of $PtCl_4{}^{2-}$ are red whereas solutions of $Pt(NH_3)_4{}^{2+}$ have negligible absorption in the visible region, and its simple salts are white. The green color can therefore be attributed to exceptional crystal effects. Atoji, Richardson, and Rundle[1] in a crystal structure determination by X-ray diffraction showed that MGS crystallizes in a tetragonal lattice with the space group *P4/mnc*, two molecular units per unit cell. In the crystals the ions stack alternately in chains along the *c* axis as shown

---

(1) M. Atoji, J. W. Richardson, and R. E. Rundle, *J. Amer. Chem. Soc.*, 79, 3017 (1957).

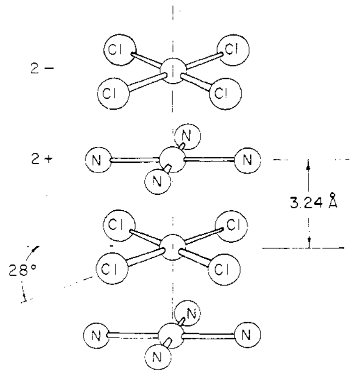

Figure 1. Alternate stacking of ions in Magnus' green salt.

in Figure 1. Furthermore, the crystals are strongly dichroic in the visible region. For light polarized in the *c* direction, a crystal may appear dark green; whereas for *a* polarization, it is very pale yellow. The compound is exceedingly insoluble in H_2O and precipitates rapidly upon the mixing of solutions of the two platinum complex ions. Cox, *et al.*,[2] noted that the indices of refraction were too great to be determined by imersion techniques but concluded that $n_\epsilon > n_\omega$.

Day, *et al.*,[3] reported single-crystal polarized spectra over 14,000-32,000 cm^{-1} with very tiny crystals. They employed the condensing lens of a microscope in their optical system, and their instrumentation was confined to room temperature. Their investigation was supplemented by Anex and coworkers[4] who obtained single-crystal, polarized, specular reflectance spectra.

For a complex with a center of symmetry, the symmetry-forbidden g ← g electronic transitions can be excited by a vibronic mechanism in which an asymmetric vibration serves as the perturbation to mix in the required odd wave functions. The intensities of such vibronic transitions are dependent upon the vibrational amplitudes, which increase with the greater excitation of higher vibrational states as the temperature rises. The transitions of $PtCl_4{}^{2-}$ in the red K_2PtCl_4 crystals exhibit a strong temperature dependence, and the band maxima at liquid helium temperatures are only 0.3-0.5 as high as at 300°K.[5]

On the other hand, there is the possibility of interionic electron-transfer transitions in MGS crystals which might have nonzero transition dipole moments. The temperature dependence of the absorption band for such a transition is quite different from one which is excited exclusively by a vibronic mechanism. When such a band narrows at lower temperatures, the relatively constant intensity may yield a peak with a higher sharper maximum. Intermolecular electron-transfer transitions were recently assigned on the basis of the temperature dependence of spectral bands for $Pt(en)Cl_2$ (en is ethylenediamine).[6] In the $Pt(en)Cl_2$ crystals the planar molecules are stacked with a separation of 3.39 Å, 0.15 Å greater than the interionic spacing of MGS. Since the striking color effect in MGS and its strong dichroism suggested strong crystal interactions, the present work was undertaken to study the temperature dependence of the crystal spectra and to determine whether any interionic electron-transfer processes could be identified.

Experimental Section

Crystals. K_2PtCl_4 was prepared by the method used in earlier work.[7] The $Pt(NH_3)_4Cl_2 \cdot H_2O$ was prepared from K_2PtCl_4 by the addition of an excess of NH_3 and boiling until all of the Magnus green salt, which formed initially, had dissolved. After excess ammonia had been boiled off and the volume reduced, the salt was precipitated by the addition of an acetone-alcohol-ether mixture. Following recrystallization it was stored in the dark.

The crystals of MGS were grown by a diffusion-controlled precipitation in a film of water between polished silica plates. Usually, finely crystallized quantities of K_2PtCl_4 and $Pt(NH_3)_4Cl_2 \cdot H_2O$, less than 1 mg each, were placed on opposite corners of one 5-cm silica plate. One drop of water was placed in the center of the plate and a second plate was pressed down on the first until the salts had dissolved. The plates were stored under a small weight in air saturated with water vapor. Crystals normally had formed in about 3 days. The plates were left in room air until most of the H_2O had evaporated, after which time they could then be easily separated. Although many small thin crystals were formed, there would sometimes be three or four large enough to cover a pinhole which was 50-100 μ in diameter. Crystals were transferred on a needle point to platinum metal pinhole plates. A small amount of silicone vacuum grease was spread near one segment of the pinhole and the crystals were pushed until one edge contacted the grease. This technique served very successfully to hold a crystal over the pinhole. The crystals were observed under a polarizing microscope to determine that they completely covered the pinhole and that there was only one crystal domain which extinguished sharply between crossed polarizers.

Instrumentation. Polarized crystal spectra were recorded by a Cary spectrophotometer, Model 14, with Glan calcite polarizers in both the reference and sample beams. It was possible to mount the pinhole plate against the copper block which formed the bottom of a vacuum-insulated can containing liquid nitrogen or helium. The actual crystal temperature could not be measured, and a nominal helium temperature of 15°K has been assigned. The comparison of a crystal of K_2PtCl_4, actually immersed in liquid helium at 4°K, did not show any greater resolved detail than the same crystal in the cryostat employed in this study.

For each crystal, a reference line was scanned with a comparable pinhole in place of the crystal. These pinholes were considerably smaller than any used in our previous work.[5,6] The individual reference lines were somewhat variable and this feature introduced a small uncertainty into the individual spectra. However, the major features of the spectra have been duplicated several times in scans for more than 15 crystals.

Spectra for two polarizations at 300 and 15°K are reproduced in Figure 2. The spectra were obtained for different crystals. The *a* polarization was for a crystal with a well-developed (001) face so that the light beam passed through the crystal along the tetragonal *c* axis which is the optic axis. This spectrum was recorded without polarizers which in themselves provide some beam attenuation. The instrument available limited the energy region to 17,000-32,000 cm^{-1}. At lower energies the instability in the optics and reduced sensitivity of the phototube precluded spectral measurements for such small crystals. It was therefore not possible to scan into a region where the absorption could be established as zero. However, the absorption appeared to be very low in *a* polarization at 5100 Å and the molar absorptivity $\epsilon_{a,5100}$ was arbitrarily set at 5 cm^{-1} M^{-1}. At this energy the absorption in *c* polarization is near a minimum and rather low, but it is somewhat higher than for *a* polarization. The value of $\epsilon_{c,5100}$ was set at 15 cm^{-1} M^{-1}. Generally, the method compares the absorbance at other wavelengths with the absorbance at this wavelength. The absorbances were converted to molar absorbancies from the thickness and the concentration of 6.28 *M* for $[Pt(NH_3)_4][PtCl_4]$ which could be calculated from the crystal density[1] of 3.77 g cm^{-3}.

Results and Discussion

Indices of Refraction. In the crystal spectra of Figure 2 it can be seen that in regions of low absorption there was a periodic fluctuation in the recorded absorbance when it was

---

(2) E. G. Cox, F. W. Pinkard, W. Wardlaw, and G. H. Preston, *J. Chem. Soc.*, 2527 (1932).

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

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

(5) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 3, 1368 (1964).

(6) D. S. Martin, Jr., L. D. Hunter, R. Kroening, and R. F. Coley, *J. Amer. Chem. Soc.*, 93, 5433 (1971).

(7) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Amer. Chem. Soc.*, 77, 2965 (1955).

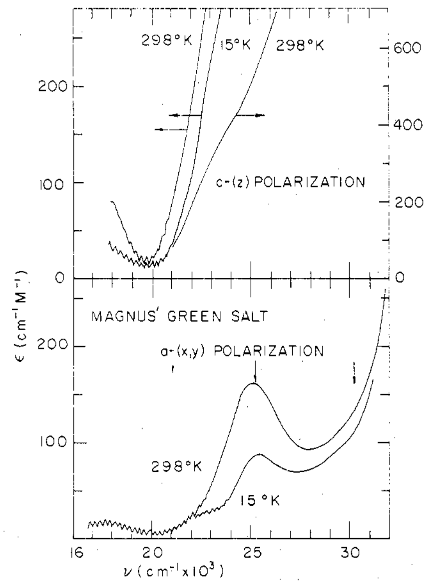

Figure 2. Polarized crystal spectrum for Magnus' green salt. For *a* polarization the light entered a (001) face of a crystal 10.6 μ thick and the spectrum was recorded without polarizer. For *c* polarization the light entered a (*hk*0) face of a crystal which was 8.1 μ thick.

plotted as a function of the wave number, $\bar{\nu}$. This periodic behavior is apparently the well-known interference effect which is observed when light is transmitted through a thin section, a few wavelengths thick with parallel faces of good optical quality. The path of the light is sketched in Figure 3 for a section of thickness L, whose surface is shown in the figure inclined to beam by an angle of incidence, θ_i. The interference bands were not observed for crystals where surface steps or different interference colors between crossed polarizers were observed. It was possible to exploit these interference effects to determine both the crystal thicknesses and their indices of refraction.

For normal incidence upon the crystal face the change in phase of light, δ_0, which suffers the reflection in the two faces, is given by the expression[8]

$$\delta_0 = 4\pi L n/\lambda^0 \qquad (1)$$

where λ^0 is the wavelength under vacuum and n is the index of refraction. The maximum transmissions (minimum absorbance) occur where $\delta_0/2\pi$ is an integer so the reflected beam interferes constructively. The transmission minima are where $\delta_0/2\pi$ is an odd number of half-integers so the reflected beam interferes destructively. A limited recording of absorbance *vs.* wavelength for *a* polarization is shown in Figure 4. This was the same crystal for which the *c* polarization is shown in Figure 2. Thus, if $\delta_0/2\pi$ is the integer N, at 5389 Å, it must be $N-1$ at 5485 Å. The equation can be written

$$N\lambda_N/n_N = (N-1)\lambda_{N-1}/n_{N-1} \qquad (2)$$

If the value of the index of refraction does not change appreciably within this wavelength region of 100 Å, the two n's cancel out in eq 2; and the value of N is determined from the two wavelength readings alone. For the two values in Figure 4 the value of 57.3 is calculated for the wavelength 5389 Å. Corresponding values of N were calculated from 11 minima and then corrected to this wavelength by adding or subtracting the number of minima difference from 5389 Å. The set of 11 minima were a region of low absorption. An average of 57.1 ± 1.0 was obtained for N. The standard deviation of 1.0 in N is consistent with an uncertainty ±2 Å in the wavelengths of the minima, which appears to be a reasonable value. It will introduce an uncertainty of *ca.* 2% into the determination of the crystal thickness.

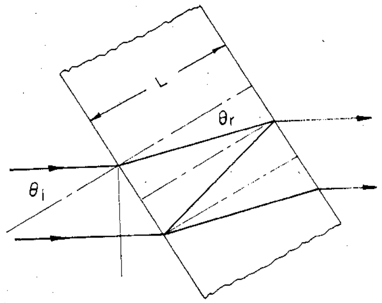

Figure 3. Optical path through a thin section.

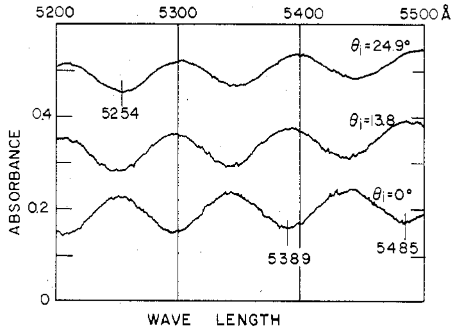

Figure 4. Recording of the absorbance for *a* polarization over a limited wavelength region with different angles of incidence. This is the same crystal whose *c*-polarized spectrum is given in Figure 2.

To obtain the thickness of the crystal from eq 1, it is necessary to have the index of refraction, for light polarized in the *a* direction. It was possible to evaluate n_a by observing the shift in the absorbance minima when a crystal in the beam was rotated about the *c* axis, its optic axis, which itself was normal to the beam. The results of such an experiment are shown in Figure 4 also. Both negative and positive rotations were employed in order to determine and correct for the tilt of the crystal on the pinhole mount. The intermediate angle of 13.8° is shown in Figure 4 to illustrate that at 24.9° the minimum for an N of 57 has been shifted to 5254 Å which is by more than one period in the interference waves. The phase delay, δ_θ, of the reflected beam from the transmitted beam for a crystal, which has been rotated by an angle θ_i, is decreased from δ_0. This decrease occurs, despite the fact that the reflected beam travels a longer path in the crystal. It is because, as can be seen in Figure 3, the portion of the upper beam in Figure 3 which is reflected interferes with the lower beam which it meets upon its second reflection. This lower beam, however, must travel further to reach the surface of the crystal. A consideration of the geometry indicates that the ratio in the phase differences is given by the expression

$$\delta_\theta/\delta_0 = \cos\theta_r \qquad (3)$$

where δ_θ is the phase difference between the reflected and incident beam with a crystal rotation θ_i and θ_r is the angle of refraction. At the wavelength of 5254 Å in Figure 4 $\delta_\theta/2\pi$ is 57; the value $\delta_0/2\pi$ is $57 + m$. From eq 2, with the assumption of constant n_a over the limited wavelength region, the value of $\delta_0/2\pi$ is $(\lambda_{57}/\lambda_{57+m})57$ = (5389 Å/5254

---

[8] M. Born and E. Wolf, "Principles of Optics," 2nd revised ed, Pergamon Press, Oxford, 1964, p 324 f.

Table I. Transitions of $PtCl_4^{2-}$ in Magnus' Green Salt Crystals[a]

$\bar{\nu}$, cm^{-1}	ϵ_{max}, cm^{-1} M^{-1}	Polarizn	Osc strength, $f \times 10^4$	Shift from K_2PtCl_4, $\Delta\bar{\nu}$, cm^{-1}	Transition assignment (ground state $^1A_{1g}$)
16,500[b]	*Ca.* 50[c] (110)	z	...	−4100	$^3A_{2g}$, ^3E_g
23,000	20	xy	2 (...)		$^3B_{1g}$?
25,200	65 (140)	xy	7.3 (20)	−1100, −4000	$^1A_{2g}$, ^1E_g
Not obsd?					$^1B_{1g}$
34,500[d]		z	Intense		$^1A_{2u}$ ($\sigma^* \leftarrow L\text{-}\pi$)

[a] Values of ϵ and f without parentheses are for 15°K. Values in parentheses are for 300°K. [b] From ref 3. [c] By extrapolation. [d] From ref 4.

Å)57. From the indicated value cos θ_r, sin θ_r can be evaluated and the index of refraction n_a will be given from Snell's law

$$n_a = \sin\theta_i/\sin\theta_r \qquad (4)$$

The average of n_a calculated from the shift of 10 minima between 4900 and 5800 Å was 1.90 ± 0.02. The uncertainty was sufficient that any wavelength dependence of n_a was not indicated. Accordingly, the thickness of this crystal could be determined with an accuracy of *ca.* ±2% to be 8.1 μ. Determination of this thickness by other means would be exceedingly difficult since its mass was only *ca.* 1 μg.

The ratio of the refractive indices was determined by the equation

$$n_c/n_a = (\delta_{5500} - \delta_{5000})_c/(\delta_{5500} - \delta_{5000})_a \qquad (5)$$

The difference in the phases could be evaluated by counting the interference waves between 5000 and 5500 Å with an interpolation proportional to $1/\lambda$ at the ends of this wavelength region. The indicated value n_c was 2.32 ± 0.03. These values for the indices of refraction are consistent with the observation by Cox, *et al.*,[2] that $n_\epsilon > n_\omega > 1.75$.

For a nonabsorbing parallel plate interferometer with r for the ratio of the reflected to incident wave amplitudes, it can be shown[8] that the ratio of the maximum transmitted light intensity to the minimum is

$$I_{max}/I_{min} = (1 + r^2)^2/(1 - r^2)^2 \qquad (6)$$

This formula applies for multiple reflections although since r is low, the higher reflections are not especially important. From Fresnel's formulas for normal incident light the value of r^2 is $(n - 1)^2/(n + 1)^2$. With the value of 1.90 for n_a, the ratio I_{max}/I_{min} is calculated to be 1.47 or log (I_{max}/I_{min}) will be 0.18. The indicated values log (I_{max}/I_{min}) obtained in Figure 4, which is the best crystal we have obtained, is 0.09. However, this value may be reduced somewhat from the theory by the absorption in the crystal.

Absorption Spectrum. The absorption bands which could be resolved from the spectra in Figure 2 are listed in Table I. It can be seen that the long-wavelength limit of our instrumentation carried just short of the maximum for a peak which Day, *et al.*,[3] placed at 16,500 cm^{-1} in c polarization. However, it is clear from the scan at 15°K that the intensity of this absorption band decreases to a considerable extent at the lower temperature. Indeed, the absorption decreases so much that the interference patterns were carried more strongly into this band, which can therefore be attributed to a vibronic excitation. The color of the crystals results from the "window" in the spectrum in the vicinity of 20,000 cm^{-1}, the green region of the visible spectrum.

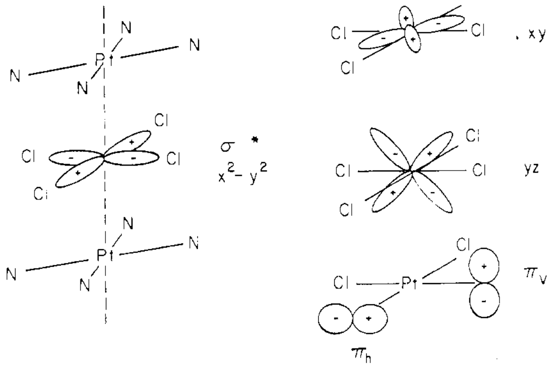

Figure 5. Angular parts of the atomic orbitals which are involved the spectral transitions.

Day, *et al.*,[3] recorded a maximum in ϵ of 300 cm^{-1} M^{-1} for c polarization at 25,000 cm^{-1} followed by a valley at 28,000 cm^{-1}. This peak and valley were directly over a peak and valley in a polarization. In the present work, as can be seen in Figure 2, the molar absorbancy increased continuously up to a value of >700 cm^{-1} M^{-1} as far as it could be followed, 26,000 cm^{-1}.

Apparently, the phototube of Day, *et al.*, was intercepting some light of the crossed polarization in their experiments. One source of such light of crossed polarization may have been the convergence of the beam by the condensing lens in their instrument. Converging light will include some polarization in the direction of the beam axis. However, it has been our experience that surface defects on the crystal scatter light with some depolarization, and this phenomenon may have been a contributing factor as well.

In a diffuse reflectance spectrum Day, *et al.*,[3] found a peak at 34,500 cm^{-1}. Anex, *et al.*,[4] found a high specular reflectance maximum for light with c polarization at just this 34,500 cm^{-1}, which must be associated with an intense absorption band. Therefore, they have concluded that a band which is at *ca.* 42,500 cm^{-1} in K_2PtCl_4 crystals with z polarization has been red-shifted to 34,500 cm^{-1}. Very likely this is a $\sigma^* \leftarrow L\text{-}\pi$ transition. The transition $^1A_{2u} \leftarrow {}^1A_{1g}$ ($b_{1g}^* \leftarrow b_{2u}$) would have this polarization. Presumably, there would also be a $\sigma^* \leftarrow L\text{-}\pi$ transition, $^1E_u \leftarrow {}^1A_{1g}$ ($b_{1g}^* \leftarrow e_u$), which would have x, y, or a polarization. For an aqueous solution of $PtCl_4^{2-}$, McCaffery, Schatz, and Stephens[9] observed an A term at 43,500 cm^{-1} in the magnetic circular dichroism spectrum which arises from an excited degenerate state, presumably this ^1E_u state. This state does not shift to lower energies in MGS as does the $^1A_{2u}$. The $d_{x^2-y^2}$ orbital, a component of σ^* (b_{1g}) is sketched in Figure 5. This orbital is concentrated in the bonding plane of the $PtCl_4^{2-}$ ion. The L-π b_{2u} orbital is a linear combination of the π_v orbitals shown in this figure. These orbitals extend out of the plane of the ion and electrons of these orbitals interact more strongly with the components of the $Pt(NH_3)_4^{2+}$ ion stacked above and below the anion than will those in the $d_{x^2-y^2}$ orbital. Thus, the electron in the orbital before the transition interacts more strongly than in the orbital following the transition. If the major interaction is the intermolecular electron repulsions, the result will be a red shift for the transition. The L-π e_u orbital is formed from the π_h orbitals shown in Figure 5. These orbitals are also concentrated in the bonding plane. Consequently, the

---

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

^1E_u state is not shifted to such low energies. The symmetry-forbidden $\sigma^* \leftarrow d$ transitions presumably borrow intensity from the allowed transitions. Since an allowed transition with z polarization has been shifted to such a much lower energy, the $\sigma^* \leftarrow d$ transitions, including the spin-forbidden ones with z polarization, have much higher intensities. The band at 16,500 cm^{-1} in c polarization with an ϵ of 80 cm^{-1} M^{-1} at 300°K correspond to the band which has been shifted about 4100 cm^{-1} from 20,200 cm^{-1}, $\epsilon = 20$ cm^{-1} M^{-1} in K_2PtCl_4. There appears to be no other transition in c polarization which can be resolved except for possibly an uncertain shoulder at 23,000-24,000 cm^{-1} from 16,500 to the intense peak at 34,500 cm^{-1}.

For the a polarization the absorption in the vicinity of 17,000 cm^{-1} was so low for crystals this thin that little can be reported about any band in this region. There was the peak with a maximum at 25,000 cm^{-1}. The value of 160 for the molar absorptivity at this energy is in good agreement with the spectrum reported by Day, *et al.*[3] This band appears to lie on the tail of an intense band which has a maximum at much higher energy than the 32,000-cm^{-1} limit of the present work. The valley at *ca.* 28,000 cm^{-1} is perhaps not as deep as in the spectrum of Day, *et al.* It can be seen from Figure 2 that when the crystal was cooled to 15°K the intensity of the peak dropped off considerably with a shift to *ca.* 25,200 cm^{-1}. Hence, it can be inferred that this band is also excited simply by the vibronic mechanism. In addition, at the lower temperature, since the bands narrow somewhat, a shoulder on the low-energy side is clearly apparent. The absorption at 15°K was resolved into gaussian components with a weak band at 23,000 cm^{-1}, ϵ 20 cm^{-1} M^{-1}, and the major band at 25,200 cm^{-1}, ϵ 65 cm^{-1} M^{-1}. The oscillator strengths of these bands are included in Table I. There is perhaps a rather large uncertainty in these oscillator strengths because the tail of the high-energy absorption still contributes a considerable intensity in this region.

For the x,y-polarized spectrum of K_2PtCl_4 there occur three maxima whose locations are shown by the arrows in Figure 2. A small band at 20,900 cm^{-1}, ϵ 10 cm^{-1} M^{-1}, has been associated with spin-forbidden transitions, based on $^3A_{2g}$ and ^3E_g states. Apparently there is a red shift of more than 4000 cm^{-1} of this peak which can be inferred from the z-c polarized spectra. The $^1A_{2g}$ state at 26,300 cm^{-1} and the ^1E_g state at 29,200 cm^{-1} in K_2PtCl_4 have coalesced in MGS to give the single peak at 25,200 cm^{-1}. These two major components of the band have not been resolved at the low temperature. Thus, the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition has apparently shifted toward the red by only *ca.* 1100 cm^{-1} whereas the $^1E_g \leftarrow {}^1A_{1g}$ transition shifted by 4200 cm^{-1}. The greater shift for the latter transition is reasonable since it can result from the greater electron repulsion of electrons in the d_{xz}, d_{yz} orbitals with the electrons on adjacent ions over that of electrons in the d_{xy} orbital, as is clear from Figure 5. An oscillator strength of 7.3×10^{-4} for the band at 25,200 cm^{-1} at 15°K agrees reasonably with the sum of 8.4×10^{-4} for the transitions to the $^1A_{2g}$ and the ^1E_g states in K_2PtCl_4, in view of the uncertainties.

The transition $^1B_{1g} \leftarrow {}^1A_{1g}$ $(d_{x^2-y^2} \leftarrow d_{z^2})$ has never been identified unambiguously on the basis of selection rules in spectra of platinum(II) complexes. Chatt, Gamlen, and Orgel[10] assigned a shoulder at 37,900 cm^{-1} on the charge-transfer bands in the solution spectrum of aqueous $PtCl_4^{2-}$ to this transition. Day, *et al.*,[3] assigned a weak shoulder at 36,500 cm^{-1} in their diffuse reflectance spectrum of K_2PtCl_4 to this transition. A similar weak shoulder at 30,000 cm^{-1} in their diffuse reflectance spectrum of MGS was also assigned to it. From the a-polarized spectrum in Figure 2, although the suggestion of a shoulder can be discerned at 29,000 to 30,000 cm^{-1}, its existence must be considered highly problematical in view of uncertainties in the reference traces. Hence, the following alternatives for this transition to the B_{1g} state seem possible. (1) The transition lies at *ca.* 30,000 cm^{-1} but is much weaker in the a polarizations than the other $d \leftarrow d$ transitions. (2) The transition lies above 32,000 cm^{-1} which is the limit of our polarized spectra.

The d_{z^2} electrons, of course, are the ones which should be the most affected by the adjacent members in the stacking chain. If interionic repulsions were the only factor, this transition would be expected to have a considerably greater red shift than other $d \leftarrow d$ transitions. If the transition to $^1B_{1g}$ occurs at 30,000 cm^{-1}, the shift would be only 6500 cm^{-1} from the K_2PtCl_4 transition and less than 4500 cm^{-1} if the transition is above 32,000 cm^{-1} as seems the more likely.

It is to be noted that the weak transition at 23,000 cm^{-1} in a polarization in MGS is rather close to the transition at 24,000 cm^{-1} with an ϵ of 7 cm^{-1} M^{-1} in K_2PtCl_4 which had been assigned primarily to $^3B_{1g} \leftarrow {}^1A_{1g}$ $(d_{x^2-y^2} \leftarrow d_{z^2})$. The presence of this transition, presumably spin forbidden at such a high energy, indicates that the d_{z^2} orbital has not been too strongly destabilized. In K_2PtCl_4 when spin-orbit coupling was included, the excited state for the 24,100 cm^{-1} band of K_2PtCl_4 was assigned[11] to the D_4' double rotational group E' (Γ_5) component of $^3B_{1g}$ whereas there was a B_2' (Γ_4) component some 3000 cm^{-1} higher. The 23,000-cm^{-1} band may therefore belong to this B_2' state. Also, with the high spin-orbit coupling of Pt it would be unlikely to have an E' state so close to the transition at 25,000 cm^{-1}. Even so, the presence of a $^3B_{1g}$ state at 23,000 cm^{-1} casts doubt upon the presence of a spin-allowed transition to the $^1B_{1g}$ state no higher than 30,000 cm^{-1} with no greater intensity than the spin-forbidden transition.

The vibronic nature of the bands which are observed in the $d \leftarrow d$ region indicates that these are normal intraionic transitions of the $PtCl_4^{2-}$ ions which have been subject to rather large crystal shifts. In this respect the present work confirms the speculation of Day, *et al.*,[3] and of Interrante and coworkers.[12,13] The absence of other than the vibronically excited transitions indicates there is no interionic electron-transfer $d \leftarrow d$ transitions which would correspond to the intermolecular electron-transfer proposed[5] for $Pt(en)Cl_2$. For the latter the excited state corresponds to an ion pair in a lattice of neutral molecules. For MGS the corresponding excited state would correspond to a pair of 1+, 1− ions in a lattice of 2+, 2− ions. Presumably, the additional lattice energy for MGS increases these transition energies beyond the region of observation.

Registry No. $[Pt(NH_3)_4][PtCl_4]$, 13820-46-7.

---

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

(11) D. S. Martin, M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 5, 1298 (1966).

(12) L. V. Interrante and F. P. Bundy, *Inorg. Chem.*, 10, 1169 (1971).

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