Polarized Crystal Absorption Spectra of Pd(II) and Pt(II) Tetrahalo and Tetrathiocyanato Complexes*

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Single crystal absorption spectra of tetrachloro, tetrabromo, and tetrathiocyanato complexes of Pd(II) and Pt(II) have been measured in the visible and near-ultraviolet region at temperatures between 10 K and 295 K. A spectral assignment of the observed d-d transitions based on ligand field theoretical calculations including electron-electron interaction and spin-orbit coupling is proposed which is consistent for all the systems investigated.

Introduction

Pt(II) and Pd(II) tend to form square planar complex ions, which crystallize in columnar structures [1]. These complex ions are stacked in columns lying parallel to one another in the crystal; the cations and, if present, the crystal water are found between the columns. The distance between the centers of neighbouring complex ions within one column is small compared with the distance found between different columns. The quasi one-dimensional nature of these structures manifests itself in a distinct dichroism in the visible and ultraviolet spectra [1, 2].

Contrary to the tetracyano compounds of Pt(II), comprehensively discussed recently, a very different optical behavior is observed with tetrahalo and tetrathiocyanato compounds [3—8]. The low energy electronic spectra of the crystalline tetracyanoplatinates show very intense bands and are distinctly different from the complex spectra in solution. This phenomenon can be explained by a strong intracolumnar interaction between the relatively close-packed tetracyano complexes (Pt-Pt distance between 2.8 Å and 3.7 Å) [5, 9].

In contrast, the tetrahalo and tetrathiocyanato crystals show electronic spectra which hardly differ from the solution spectra with regard to the peak energies and intensities of the absorption bands apart from polarization effects. These facts suggest that the crystalline tetrahalo and tetrathiocyanato compounds can be treated as an "oriented gas" of complex ions. This picture is supported by the relatively large intracolumnar metal-metal distances (>4 Å) in the tetrahalo [7, 10] and tetrathiocyanato* compounds and the resulting reduction of the intermolecular interaction.

Experimental Results

Single crystal absorption spectra of the compounds

K_2PtCl_4	$K_2PdBr_4 \cdot 2\,H_2O$
K_2PtBr_4	$K_2Pt(SCN)_4$
K_2PdCl_4	$K_2Pd(SCN)_4$

were measured in the spectral range from 12000 cm^{-1} to 35000 cm^{-1} at temperatures between 10 K and 295 K. The incident light was linearly polarized with orientations of the electric field vector $\boldsymbol{E}$ parallel to the extinction directions of the crystals**.

The preparation of the compounds was performed according to known methods [11], the purity of the products being checked by elemental analysis and measurements of the solution spectra.

The crystals were grown by slow evaporation of saturated solutions at room temperature. The solutions of the tetrahalo complexes contained an excess of Cl^- and Br^- ions. Thin crystals up to a thickness of ca. 50 μ were obtained by evaporation of a small drop of solution on a quartz disc. The crystals always presented a crystal face containing the crystallographic c-axis.

The absorption spectrometer is an apparatus particularly developed for investigations of very

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* The crystal data of $K_2Pd(SCN)_4$ and $K_2Pt(SCN)_4$ are the same within the uncertainty of the measurements (about 1%): $a = 11.0$ Å, $b = 12.9$ Å, $c = 4.2$ Å, and $\beta = 98°$. We thank Dr. U. Klement, Universität Regensburg, for making the single crystal X-ray investigations.

** $E \parallel c$ yields the π-spectra, $E \perp c$ the σ-spectra, with c being the crystallographic axis.

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small single crystals with polarized light [5]. The substantial features of this spectrometer are a xenon extra-high pressure arc, a monochromator, Spex model 1401, a microscope-like optical system, a glan polarization prism, a beam splitter, and two photomultipliers, EMI type 9558 QB. Before every run of a measurement a zero line (without a crystal in the sample beam) was obtained for corrections of the sample curves. To cool down the crystals, a helium evaporation cryostat was used lowering the temperature of the samples to ca. 10 K [12].

On the long-wavelength side of the absorption spectra there are weak bands ($\varepsilon_{\max} \approx 200$ l/mol cm) which show the characteristic features of d-d transitions with regard to their low intensity and temperature behavior (increase of intensity with increasing temperature). The observed absorption bands are sometimes located in the tail of the strongly absorbing charge-transfer transitions. These charge-transfer bands are π(ligand) → d(central ion) transitions and occur at lower energy with Pd(II) complexes than with Pt(II) complexes due to the greater ionization energy of Pd(I) compared to that of Pt(I). The peak energies of the observed bands are given in Table 1.

K_2PtCl_4:

The results of measurements with *thin* crystals (Fig. 1) are in good agreement with those of Martin et al. [6]. Additionally, a spectrum of a *very thick* crystal shows distinct double vibrational fine structure in both polarization directions around 24000 cm^{-1} (Figure 2). The period is 290 cm^{-1} in both progressions. Whereas in the σ-directions the progressions are separated by 140 cm^{-1}, the displacement of the progressions is 110 cm^{-1} in the π-direction.

The lowest absorption bands are located at 17500 cm^{-1} and 18000 cm^{-1}. The emission of K_2PtCl_4 is found [13] at ca. 13000 cm^{-1}, therefore the Stokes shift amounts to ca. 5000 cm^{-1}. Using the equation [14]

$$\Delta = \frac{H(T=0)^2}{\hbar\,\omega \cdot 4 \cdot \ln 2}$$

where Δ is the Stokes shift, $H(T=0)$ is the half-width at $T=0$ and $\hbar\omega$ is the vibrational energy of the normal mode involved in the progression, the Stokes shift is found to be in good agreement with the half-width of the absorption bands estimated to be approximately 2000 cm^{-1}.

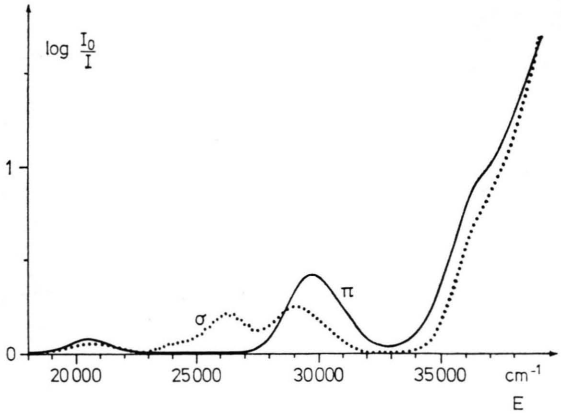

Fig. 1. Single crystal absorption spectrum of K_2PtCl_4 at 10 K. Crystal thickness ca. 15 μ.

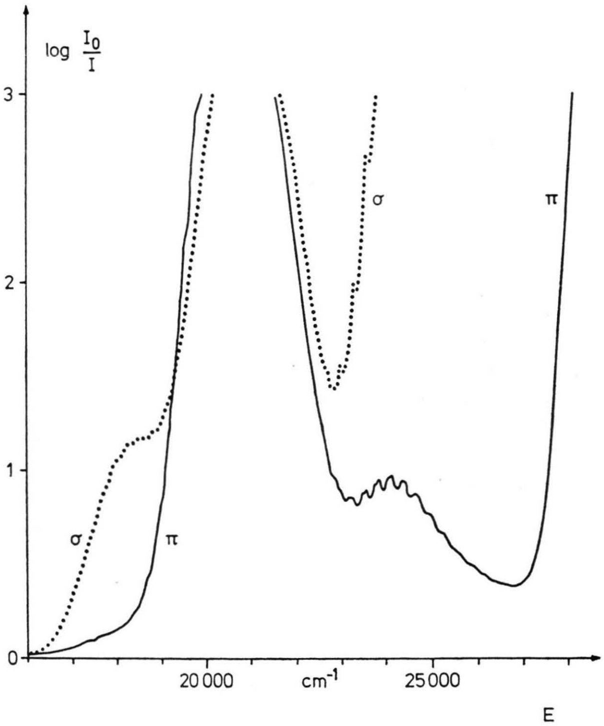

Fig. 2. Single crystal absorption spectrum of K_2PtCl_4 at 10 K. Crystal thickness ca. 0.8 mm.

K_2PtBr_4:

With K_2PtBr_4 only a thick crystal was investigated (Fig. 3); the thin crystal measurements were taken from Martin et al. [7]. A double vibrational fine structure in the 22800 cm^{-1} band in the π-spectrum analogous to that in the corresponding absorption band of K_2PtCl_4 cannot be determined

Table 1. A comparison of the calculated transition energies with the observed peaks. The theoretical values of $K_2Pt(SCN)_4$ are calculated on the basis of the "strong field approximation". a) taken from [7]. b) taken from [8].

K_2PtCl_4		K_2PtBr_4		$K_2Pt(SCN)_4$		K_2PdCl_4		$K_2PdBr_4 \cdot 2H_2O$		$K_2Pd(SCN)_4$		Transition
experimental T = 10K [cm^{-1}]	calculated Dq = 2600 Ds = 3900 F_2 = 410 F_4 = 16 ζ = 1360 [cm^{-1}]	experimental T = 10K [cm^{-1}]	calculated Dq = 2440 Ds = 3500 F_2 = 355 F_4 = 14 ζ = 1000 [cm^{-1}]	experimental T = 10K [cm^{-1}]	calculated Dq = 2370 Ds = 4400 F_2 = 400 F_4 = 15 [cm^{-1}]	experimental T = 10K [cm^{-1}]	calculated Dq = 2340 Ds = 4950 F_2 = 600 F_4 = 46 [cm^{-1}]	experimental T = 10K [cm^{-1}]	calculated Dq = 2160 Ds = 4635 F_2 = 575 F_4 = 40 [cm^{-1}]	experimental T = 10K [cm^{-1}]	calculated Dq = 2260 Ds = 5050 F_2 = 595 F_4 = 56 [cm^{-1}]	$\Gamma_1^+(^1A_{1g}) \rightarrow$
π : 17500 σ : 18000	17400	π : 16200 σ : 16700	16100	π : 19700 σ : 19700	18900	π : 17100 σ : 17700	17200	π : 15700 σ : 17000 b)	16000		17000	$\Gamma_4^+(^3B_{1g})$
												$\Gamma_5^+(^3B_{1g})$
π : 20700 σ : 20900	20900	π : 18900 σ : 19100	19200	π : 23500 σ :	22500	π : 23400 σ : 23400	23400	π : 21800 σ : 21800	21800	π : 23300 σ :	23400	$\Gamma_3^+(^1B_{1g})$
	23700		22500		22100		18600	π : 17400 σ : b)	17400	π : 16700 σ : 16700	16700	$\Gamma_1^+(^3A_{2g})$
π : 24000 σ :	24100	π : 22800 σ :	22700									$\Gamma_5^+(^3A_{2g})$
π : - σ : 26200	26500	π : - σ : 24400 a)	24600	π : (23900) σ : 23900	23200	π : - σ : 21800	21800	π : - σ : 20200	20200	π : (20600) σ : 20600	20600	$\Gamma_2^+(^1A_{2g})$
	26100		24200		25600		23400		21800		22600	$\Gamma_1^+(^3E_g)$
π : - σ : 24000	24300	π : - σ : 22700 a)	22900	π : (21600) σ : 21600								$\Gamma_2^+(^3E_g)$
	27000		24800									$\Gamma_3^+(^3E_g)$
	26800		24700									$\Gamma_4^+(^3E_g)$
	26100		24200									$\Gamma_5^+(^3E_g)$
π : 29300 σ : 28700	29300	π : 27400 σ : 26800 a)	27000	π : 27200 σ : 26600	28600	in solution 30 100	28800	π : 27100 σ :	26800	π : 28500 σ :	28400	$\Gamma_5^+(^1E_g)$

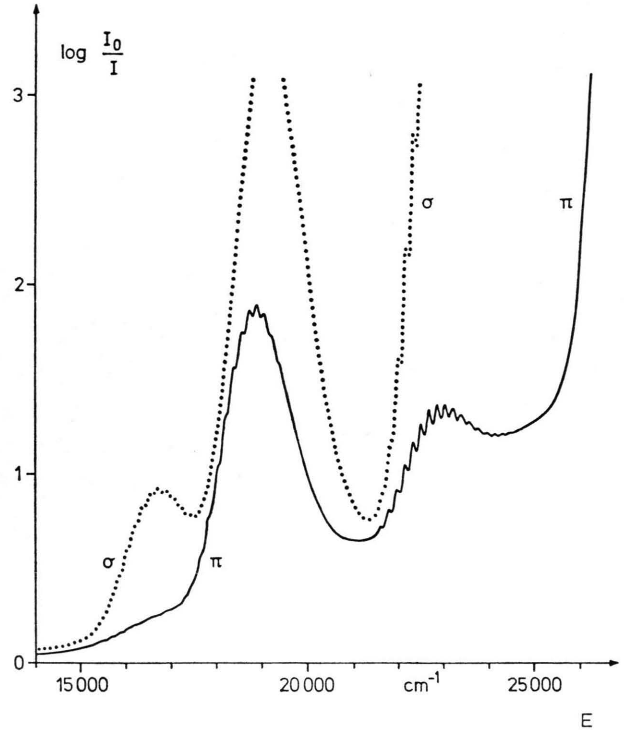

Fig. 3. Single crystal absorption spectrum of K_2PtBr_4 at 10 K. Crystal thickness ca. 0.8 mm.

with any certainty. The emission of the tetrabromoplatinate shows a maximum at ca. 12000 cm^{-1} [13]. If it is assumed that the emission results from the excited terms assigned to the bands at 16200 cm^{-1} and 16700 cm^{-1}, the Stokes shift has the same value as in K_2PtCl_4.

K_2PdCl_4:

Both the 17700 cm^{-1} and the 21800 cm^{-1} band in the σ-spectrum show a double vibrational fine structure. The separation of the two progressions are 135 cm^{-1} in the 17700 cm^{-1} band and 100 cm^{-1} in the 21800 cm^{-1} band. The emission maximum of K_2PdCl_4 lies slightly below 11600 cm^{-1} [13]. If the corresponding absorptions are taken to be the 17100 cm^{-1} and 17700 cm^{-1} bands, one obtains a slightly greater Stokes shift in the palladium complex than in the analogous platinum complex. This fact is consistent with the observed half-widths of the bands, being several 100 cm^{-1} greater in K_2PdCl_4.

$K_2PdBr_4 \cdot 2\,H_2O$:

Crystals of the tetrabromo complex grown in aqueous solution are dihydrates, but at room temperature the crystal water is easily lost. To avoid loss of water resulting in crystal destruction, the crystals were mounted in the cryostat in a room maintained at 0 °C, then they were immediately cooled to low temperatures. The spectra of thin crystals obtained in this way are in good agreement with those of Martin et al. [8] obtained with K_2PdBr_4 crystals having no crystal water. The tetrabromopalladate(II) emission has not been investigated as yet.

$K_2Pt(SCN)_4$:

The $K_2Pt(SCN)_4$ spectrum (Fig. 4) also shows a distinct dichroism; totally polarized bands cannot be observed, however, as with $K_2Pd(SCN)_4$. The greatest degree of polarization occurs in the 23900 cm^{-1} band of the σ-spectrum. Therefore, this band may correspond with the 24400 cm^{-1} band in the K_2PtBr_4 spectrum which is totally polarized in the σ-direction. Then the absorption bands at 26600 cm^{-1} and 27200 cm^{-1} can be correlated with the K_2PtBr_4 bands at 26800 cm^{-1} and 27400 cm^{-1}. The shoulder at 21600 cm^{-1} can also be compared with a shoulder in the K_2PtBr_4 spectrum observed at 22700 cm^{-1} and σ-polarized as well. The maximum of the rather strong $K_2Pt(SCN)_4$ emission lies at 14600 cm^{-1} [15], thus shifted by 2600 cm^{-1} to higher energy in comparison to K_2PtBr_4. On the assumption that the emission results from the

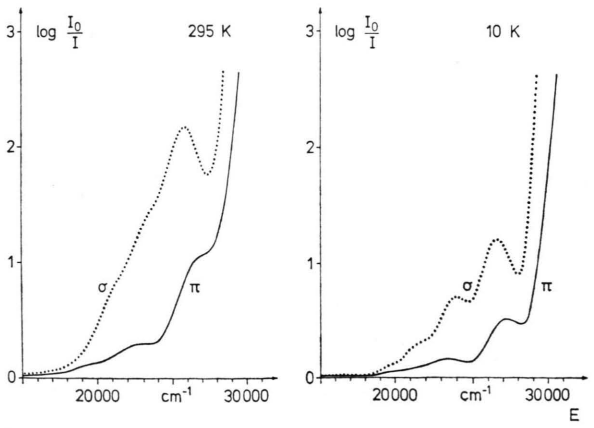

Fig. 4. Single crystal absorption spectra of $K_2Pt(SCN)_4$ at 295 K and 10 K. Crystal thickness ca. 15 μ.

excited terms assigned to the absorption at 19700 cm^{-1}, the same Stokes shift value of ca. 5000 cm^{-1} is obtained as with the tetrahalo complexes of Pt(II).

$K_2Pd(SCN)_4$:

Like the tetrahalo complexes of Pd(II), $K_2Pd(SCN)_4$ also shows a σ-polarized absorption band (not totally, but with a high degree) (Figures 5 and 6). The maximum is located at the same energy as in the tetrabromopalladate. On the low energy side of this band a weak absorption is obtained in both polarization directions. The shoulder in the π-spectrum at 23300 cm^{-1} may correspond to the relatively weak 21800 cm^{-1} band in the K_2PdBr_4 spectrum. No tetrathiocyanatopalladate emission has been observed (sample temperature $\geqq 77$ K) contrary to K_2PdCl_4 [15].

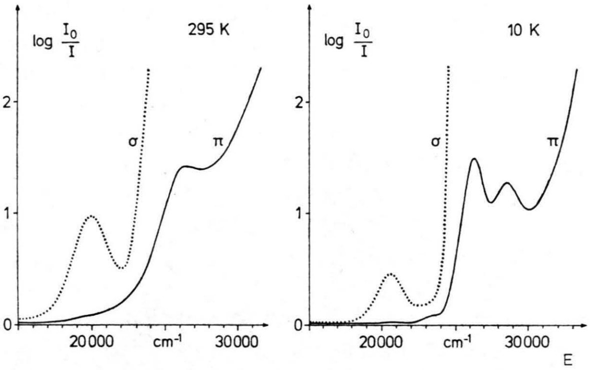

Fig. 5. Single crystal absorption spectra of $K_2Pd(SCN)_4$ at 295 K and 10 K. Crystal thickness ca. 15 μ.

Discussion

In the past, several procedures were used to interpret the spectra of square planar d^8 complexes. Basch and Gray [16] as well as Cotton and Harris [17] have used a semi-empirical one-electron MO scheme. Calculations according to the scattered wave Xα-method were made by Messmer, Interrante, and Johnson (for $PtCl_4^{2-}$ and $PdCl_4^{2-}$) [18]. Fenske, Martin, and Rüdenberg [19] proposed a ligand field theoretical treatment of the multielectron system. In the following the observed spectra are interpreted on the basis of ligand field theory including electron-electron interaction and spin-orbit coupling. The crystal is treated as an "oriented gas" since the square planar complex

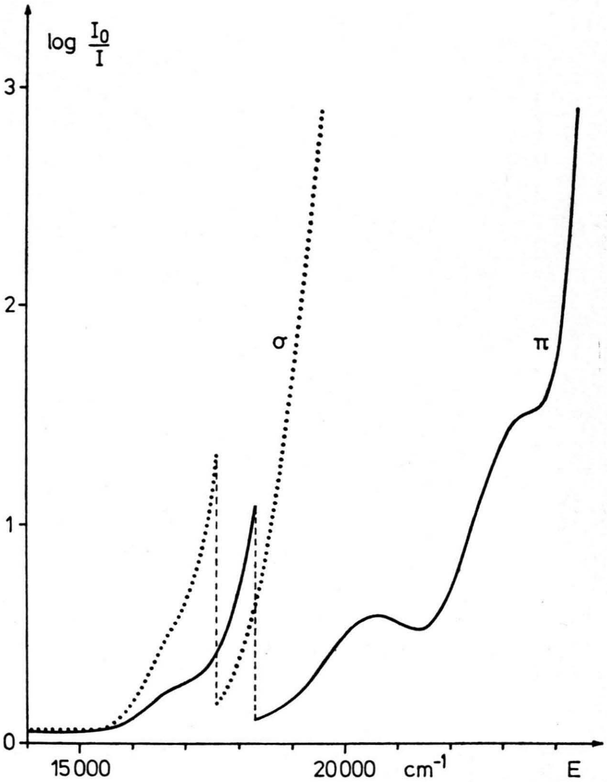

Fig. 6. Single crystal absorption spectrum of $K_2Pd(SCN)_4$ at 10 K. Crystal thickness ca. 0.3 mm, below 17600 cm^{-1} and 18000 cm^{-1} ca. 1.3 mm.

ions are oriented with their normal to the plane having no intermolecular interactions. The problem is thus reduced to that of a single complex ion.

The one-electron terms of the central ion $a_{1g}(d_{z^2})$, $b_{1g}(d_{x^2-y^2})$, $b_{2g}(d_{xy})$, and $e_g(d_{xz}, d_{yz})$ for the symmetry group D_{4h} have the following energies [5, 20]:

$$\varepsilon(a_{1g}) = \frac{18}{7} Dq - 2Ds\,,$$

$$\varepsilon(b_{1g}) = \frac{38}{7} Dq + 2Ds\,,$$

$$\varepsilon(b_{2g}) = -\frac{32}{7} Dq + 2Ds\,,$$

$$\varepsilon(e_g) = -\frac{12}{7} Dq - Ds\,.$$

Figure 7 shows the dependence of these energies upon the Ds/Dq ratio. This ratio determines the order of the one-electron terms. With platinum complexes, the Ds/Dq value should be between 1

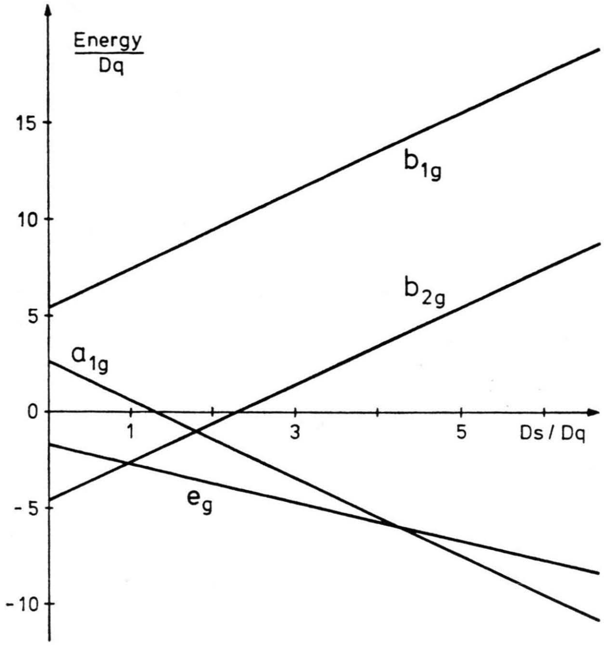

Fig. 7. The energy order of the d-terms depending upon the Ds/Dq ratio.

and 3, with palladium complexes it is between 2 and 4*.

Corresponding to the electronic configuration $a_{1g}^2 b_{2g}^2 e_g^4$ the multi-electron ground state is $^1A_{1g}$. Thus, the following one-electron transitions can be observed**:

$$a_{1g} \to b_{1g} \quad {}^1A_{1g}(\Gamma_1^+) \to \begin{cases} {}^1B_{1g}(\Gamma_3^+) \\ {}^3B_{1g}(\Gamma_4^+ + \Gamma_5^+); \end{cases}$$

$$b_{2g} \to b_{1g} \quad {}^1A_{1g}(\Gamma_1^+) \to \begin{cases} {}^1A_{2g}(\Gamma_2^+) \\ {}^3A_{2g}(\Gamma_1^+ + \Gamma_5^+); \end{cases}$$

$$e_g \to b_{1g} \quad {}^1A_{1g}(\Gamma_1^+) \to \begin{cases} {}^1E_g(\Gamma_5^+) \\ {}^3E_g(\Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ \\ \qquad + \Gamma_4^+ + \Gamma_5^+)\,. \end{cases}$$

In the complete ligand field theoretical multi-electron problem, several secular determinants (maximum size 20×20) appear for reasons of symmetry. Their elements are dependent upon the two ligand field parameters Dq and Ds, the Slater parameters F_2 and F_4, and the spin-orbit coupling constant ζ [21].

A computer program [22] was used to diagonalize the energy matrices***. The parameters Dq, Ds, F_2, F_4 and ζ were varied for every investigated system with the aim to obtain an optimal fitting of the calculated transition energies to the observed peaks. Additionally, the aim was to get a spectral assignment as consistent as possible for all investigated systems.

The d-d transitions are Laporte forbidden and require "intensity borrowing" through coupling to odd vibrations. The only odd vibrations of square planar complexes have the symmetries α_{2u}, β_{2u}, and ε_u. Thus, for linearly polarized light and taking into account the ground state being $^1A_{1g}(\Gamma_1^+)$, only those excitations are allowed which are given in Table 2. For example, transitions to the Γ_2^+ and Γ_4^+ states are totally polarized in the σ-direction.

K_2PtCl_4:

Good agreement was obtained between the observed peaks and the transition energies calculated by diagonalizing the complete energy matrix using the parameters $Dq = 2600$ cm^{-1}, $Ds = 3900$ cm^{-1}, $F_2 = 410$ cm^{-1}, $F_4 = 16$ cm^{-1}, and $\zeta = 1360$ cm^{-1}, see Table 1.

The totally σ-polarized absorption band at 26100 cm^{-1} has to be assigned to the $^1A_{1g} \to {}^1A_{2g}$ transition. This assignment is based on the high band intensity indicating that this band arises from a spin-allowed transition. Of the three possible spin-allowed transitions, only the one to $^1A_{2g}$ is σ-polarized.

The result of magnetic circular dichroism measurements [23] with K_2PtCl_4 enables the band with maxima at 28700 cm^{-1} and 29300 cm^{-1} (depending on polarization) to be assigned to the $^1A_{1g} \to {}^1E_g$ transition. The third spin-allowed transition $^1A_{1g} \to {}^1B_{1g}$ corresponds to the band located at 20700 cm^{-1} and 20900 cm^{-1}.

The shoulder in the $^1A_{2g}$ band occuring at 24000 cm^{-1} must arise from excitation of the $\Gamma_2^+(^3E_g)$ component of the ^3E_g term. According to the selection rules, this transition is also polarized

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* If the Ds/Dq ratio is calculated with Slater radial functions (Z_{eff} and n^* according to Slater rules), one obtains, using the point charge model and with a central ion-ligand distance of 4 a.u., a value of 3.0 for Pt(II) and 3.7 for Pd(II). With hydrogen-like functions one gets $Ds/Dq = 0.9$ for Pt(II) and $Ds/Dq = 2.2$ for Pd(II).

** The components, obtained after having taken into account the spin-orbit coupling, are added to the LS terms in brackets using the nomenclature of Bethe.

*** Including electron-electron interaction and spin-orbit coupling.

in the σ-direction. Due to exchange interaction and spin-orbit coupling, the transition energy of this component has to be several thousand wavenumbers smaller than that of the corresponding singlet transition ${}^1E_g$. Thus the $\Gamma_2{}^+({}^3E_g)$ absorption must occur in the vicinity of the ${}^1A_{2g}$ band. Both absorptions appear with comparable intensity because the wave-functions of $\Gamma_2{}^+({}^3E_g)$ and ${}^1A_{2g}$ are mixed considerably by spin-orbit coupling due to the small energy difference between the terms.

The absorption at 24000 cm^{-1} in the π-spectrum showing a very distinct double vibrational fine structure, can be assigned to the $\Gamma_5{}^+({}^3A_{2g})$ transition. The appearance of this double vibrational fine structure supports the assignment of the band to a $\Gamma_5{}^+$ term. In the present case, a double vibrational fine structure will only appear if an odd normal mode of ε_u symmetry is needed for the intensity borrowing mechanism of the parity forbidden transitions considered (compare Ref. [8]), because in square planar complexes there are two ε_u vibrations which ordinarily have different energies. In the ground state this energy difference is 129 cm^{-1} with K_2PtCl_4. Therefore the transitions involving both ε_u vibrations should show two vibrational progressions separated by the energy difference of these ε_u vibrations. With a $\Gamma_1{}^+({}^1A_{1g})$ ground state only transitions to $\Gamma_5{}^+$ terms are allowed by these vibrations in the π-direction (see Table 2). Around 24000 cm^{-1}, a $\Gamma_5{}^+({}^3A_{2g})$ and $\Gamma_5{}^+({}^3E_g)$ are expected. Both states are mixed however by spin-orbit coupling with a slightly greater ${}^3A_{2g}$ component in the lower state.

The weak absorptions at 17500 cm^{-1} and 18000 cm^{-1} are assigned to transitions to the $\Gamma_5{}^+$ and $\Gamma_4{}^+$ components of ${}^3B_{1g}$, respectively. The considerably higher intensity at 18000 cm^{-1} in the σ-spectrum may be explained by the fact that the transition to $\Gamma_4{}^+({}^3B_{1g})$ is totally σ-polarized according to the selection rules and apparently more intense than the $\Gamma_5{}^+({}^3B_{1g})$ component, which appears in both polarization directions.

Table 2. Selection rules for vibronically allowed transitions in square planar complexes.

	Γ_1^+	Γ_2^+	Γ_3^+	Γ_4^+	Γ_5^+
α_{2u}	π	–	–	–	σ
β_{2u}	–	–	π	–	σ
ε_u	σ	σ	σ	σ	π

Hence, seven transition energies calculated with the above values of the five parameters Dq, Ds, F_2, F_4, and ζ are quantitatively in good agreement with the observed energies. For the other five theoretical transitions — all spin-forbidden — no corresponding absorption bands are observed.

The Ds/Dq ratio is 1.5, thus lying in the range between 1 and 3 expected for a Pt(II) central ion. The Slater parameters F_2 and F_4 for the free Pt(II) ion are unknown. A value of ca. 600 cm^{-1} has been estimated for the difference $F_2 - 5F_4$ [24]. With the $PtCl_4{}^{2-}$ complex, this difference amounts to 330 cm^{-1}, or 45% less than with the free Pt(II) ion. A nephelauxetic effect of the same order is also found with the $IrCl_6{}^{3-}$ complex ion [25]. The spin-orbit coupling constant of the free Pt(II) is also unknown. A value of the same order as that of the Pt(I) ion has to be expected ($\zeta = 3368$ cm^{-1}) [26]. The comparably small value of ζ obtained with the complex demonstrates a strong relativistic nephelauxetic effect.

K_2PtBr_4:

With K_2PtBr_4, the calculated transition energies are also in good agreement with the observed ones. They are given in Table 1, calculated using $Dq = 2440$ cm^{-1}, $Ds = 3500$ cm^{-1}, $F_2 = 355$ cm^{-1}, $F_4 = 14$ cm^{-1}, and $\zeta = 1000$ cm^{-1}. The K_2PtBr_4 spectrum is very similar to that of K_2PtCl_4. The tetrachloroplatinate interpretation can therefore be applied to the K_2PtBr_4 system.

As expected, the Dq of tetrabromoplatinate is somewhat smaller than that of K_2PtCl_4. The Ds/Dq ratio is found to be 1.43, thus being almost as great as that of K_2PtCl_4. Slightly smaller values are obtained for the Slater parameters and the spin-orbit coupling constant, showing a somewhat greater nephelauxetic effect with the $PtBr_4{}^{2-}$ complex.

K_2PdCl_4:

The calculated values given in Table 1 are obtained with the parameter set $Dq = 2340$ cm^{-1}, $Ds = 4950$ cm^{-1}, $F_2 = 600$ cm^{-1}, and $F_4 = 46$ cm^{-1}. The value of the spin-orbit coupling constant cannot be determined by the observed absorptions because the terms assigned to the individual bands are mixed only a little, if at all, by spin-orbit coupling.

The totally σ-polarized absorption band at 21800 cm^{-1} is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in accordance with its polarization and intensity. The second band with appreciable intensity located at 23400 cm^{-1} has to be correlated with the $^1B_{1g}$ transition. The weak absorptions at 17100 cm^{-1} and 17700 cm^{-1} arise from transitions to the Γ_5^+ and Γ_4^+ components of the $^3B_{1g}$ term analogous to the platinum complexes. This assignment is reasonable because these absorptions show the same polarization and intensity as the $^3B_{1g}$ absorptions of the platinum complexes. Thus, compared to the platinum complex, the order of the singlet terms $^1A_{2g}$ and $^1B_{1g}$ is changed, whereas that of the corresponding triplet terms $^3A_{2g}$ and $^3B_{1g}$ is not.

The Ds/Dq ratio amounting to 2.12 is greater than with the platinum complexes and lies in the expected range between 2 and 4. The Dq value is smaller than with the analogous platinum complex as expected. On the contrary, the Slater parameters are distinctly greater, but this is also expected when comparing a second row to a third row metal ion. The difference $F_2 - 5F_4$ is 60% smaller than the value of the free Pd(II) ion. A decrease of approximately the same order in the Slater parameters due to the nephelauxetic effect is found for $RhCl_6^{3-}$ [25].

No crystal absorption could be observed at the energies calculated for the ^1E_g and ^3E_g terms. Martin et al. [8] however, have found in the $PdCl_4^{2-}$ solution spectrum a relatively intense absorption at 30100 cm^{-1}, which may correspond to the $^1A_{1g} \rightarrow {}^1E_g$ transition. The spin-forbidden transition to $^3A_{2g}$ could also not be observed in the crystal spectra.

$K_2PdBr_4 \cdot 2\,H_2O$:

With $Dq = 2160$ cm^{-1}, $Ds = 4635$ cm^{-1}, $F_2 = 575$ cm^{-1} and $F_4 = 40$ cm^{-1}, the transition energies given in Table 1 are obtained. The assignment of the absorption bands is analogous to that of K_2PdCl_4.

The transition energies calculated using the above parameters are in good agreement with those measured. The assignment of the 27100 cm^{-1} band to the $^1A_{1g} \rightarrow {}^1E_g$ transition seems to be uncertain for the intensity of this band does not increase with increasing temperature as is usual for d-d transitions. This band may arise from a forbidden charge-transfer transition.

In a comparison of the two parameter sets for the tetrahalopalladate complexes, Dq of the tetrabromo complex is smaller, whereas the Ds/Dq ratio, 2.15 with $K_2PdBr_4 \cdot 2\,H_2O$, has approximately the same value in both complexes. With the tetrabromo complex one obtains somewhat smaller Slater parameters than with K_2PdCl_4. The same results are found in the comparison of both tetrahaloplatinates.

$K_2Pd(SCN)_4$:

The transition energies calculated with $Dq = 2260$ cm^{-1}, $Ds = 5050$ cm^{-1}, $F_2 = 595$ cm^{-1}, and $F_4 = 56$ cm^{-1} and those determined experimentally are given in Table 1.

The strongly σ-polarized band at 20600 cm^{-1} is assigned to the $^1A_{2g}$ transition in accordance with its polarization and intensity. The transition to $^1B_{1g}$ corresponds to the 23300 cm^{-1} band, so that the energy difference between $^1A_{2g}$ and $^1B_{1g}$ is about 1100 cm^{-1} greater with $K_2Pd(SCN)_4$ than with the analogous tetrahalo complexes. This must be a result of the greater Ds/Dq ratio of 2.23.

A consequence of the greater Ds/Dq ratio is an exchange of the order of the triplet terms $^3B_{1g}$ and $^3A_{2g}$ in comparison to that of the tetrahalo complexes. Therefore the weak absorption at 16700 cm^{-1} must be assigned to the $^3A_{2g}$ transitions. This assignment is supported by the fact that this absorption shows less intensity and a different polarization behavior than the lowest absorptions of the tetrahalo complexes. Additionally, with $^3A_{2g}$ being the lowest term instead of $^3B_{1g}$, the changed emission behavior of $K_2Pd(SCN)_4$ compared to the tetrachloropalladate may be explained.

The ^1E_g transition is assigned to the 28500 cm^{-1} absorption. The band at 26200 cm^{-1} may be a σ-polarized charge transfer transition appearing in the π-spectrum with weak intensity due to insufficient polarization. This band does not behave like a d-d transition since the intensity does not grow with increasing temperature.

$K_2Pt(SCN)_4$:

It is impossible to get values for the five parameters Dq, Ds, F_2, F_4, and ζ which are in satisfactory *quantitative* agreement with the peaks observed in the crystal spectrum of $K_2Pt(SCN)_4$. As an example, transition energies with $Dq = 2370$ cm^{-1}, $Ds = 4400$ cm^{-1}, $F_2 = 400$ cm^{-1}, and $F_4 = 15$ cm^{-1} are given in Table 1. The reason for this lack of agreement may be that the ligand field theoretical approximation is too rough. It is still sufficient to make an assignment of the observed absorption bands.

The strongly σ-polarized band at 23900 cm^{-1} has to be assigned to the transition to $^1A_{2g}$. The absorptions at 26600 cm^{-1} and 27200 cm^{-1} arise from the transition to ^1E_g. The transition to the $\Gamma_2{}^+$ component of ^3E_g, which has a strong interaction with $^1A_{2g}$ by spin-orbit coupling, lies at 21600 cm^{-1}. The absorptions at 23500 cm^{-1} and 19700 cm^{-1} correspond to the transitions to the $^1B_{1g}$ and $^3B_{1g}$ terms, respectively.

This assignment is based on a greater Ds/Dq ratio compared to that of the tetrahaloplatinates, as found in the corresponding palladium complexes. With $K_2Pt(SCN)_4$ the Ds/Dq value increases to such an extent that the emission peak of this complex compared with K_2PtCl_4 is shifted to higher energy by 1600 cm^{-1} although the Dq of $K_2Pt(SCN)_4$ is smaller than that of K_2PtCl_4. Since only the $^3B_{1g}$ term depends upon the Ds/Dq ratio to the degree observed in the emission spectra, the proposed assignment is supported by the emission behavior.

Conclusion

By means of single crystal absorption spectra and multi-electron calculations based on ligand field theory, an assignment of the d-d transitions of tetrachloro, tetrabromo, and tetrathiocyanato complexes of Pd(II) and Pt(II) has been made. The agreement of the calculated transition energies with the observed band maxima allows a new spectral assignment to be made which is consistent regarding the Ds/Dq ratios and the values of F_2, F_4, and ζ.

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