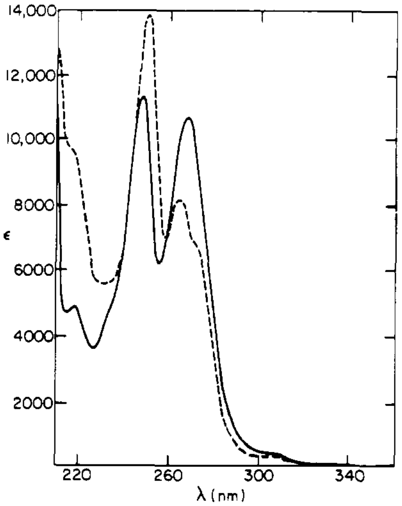

Figure 6. Electronic absorption spectrum of *trans*-[Pt(PEt$_3$)$_2$Cl$_2$] in CH$_3$CN (—) and 7/4 methylcyclohexane/pentane (- - -) solution at 298 K.

coordination is d_{z^2} which should be destabilized in the solvated complex. Hence MLCT transitions which involve depopulation of this orbital will lie at lower energy in CH$_3$CN than in the noninteracting hydrocarbon solvents. Band II is a single peak (3.74 μm^{-1}) in CH$_3$CN solution but is resolved into two components in hydrocarbon solution (Figure 6 and Table I). The IIb peak at 3.80 μm^{-1} in hydrocarbon solution is attributed to the $^1[d_{z^2} \rightarrow \pi^*]$ transition from the MCD data, and indeed it does shift to lower energy (3.74 μm^{-1}) in CH$_3$CN solution. The $^3[d_{yz} \rightarrow \pi^*]$ transition seen as a shoulder (IIa) at 3.70 μm^{-1} in hydrocarbon solution apparently blue shifts to 3.74 μm^{-1} in CH$_3$CN solution, implying partial stabilization of the d_{yz} orbital via π interaction with the weakly π-accepting CH$_3$CN. The *trans*-[Pt(PEt$_3$)$_2$Br$_2$] complex appears to show a similar solvent shift, but the effect is largely masked by the presence of the intense π-LMCT band in this spectral region (Table I). It is interesting that none of the other complexes examined in this work show such a solvent effect, but we can offer no explanation for this observation.

Finally, the results described herein are relevant to a recent photochemical study of related complexes. Costanzo et al.[19] recently reported that *cis*- and *trans*-[Pt(PEt$_3$)$_2$(Ph)Cl] undergo photoinduced cis $\rightleftarrows$ trans isomerization in acetonitrile solution. Quantum yields were measured, and the observed wavelength effects were rationalized on the basis of the different excited states involved. The latter were deduced from an interpretation of the electronic absorption spectra of these derivatives in which the observed bands were attributed to LF and LMCT transitions. However, the electron absorption spectra of *cis*-[Pt(PEt$_3$)$_2$(Ph)Cl] (λ 280 nm, ϵ 1600 M^{-1} cm^{-1}; λ 245 nm, ϵ 990 M^{-1} cm^{-1})[19] and *trans*-[Pt(PEt$_3$)$_2$(Ph)Cl] (λ 290 nm, ϵ 1250 M^{-1} cm^{-1}; λ 255 nm, ϵ 5300 M^{-1} cm^{-1})[19] are virtually identical with those of the *cis*- and *trans*-[Pt(PEt$_3$)$_2$(Me)Cl] complexes studied herein (Table I) for which the observed bands have been assigned as MLCT transitions. Common MLCT assignments for the observed bands in the *cis*- and *trans*-[Pt(PEt$_3$)$_2$(Ph)Cl] complexes are thus indicated. The excited-state arguments given by Costanzo et al.[19] to rationalize their photochemical results are therefore inappropriate, and the observed photochemistry of the *cis*- and *trans*-[Pt(PEt$_3$)$_2$(Ph)Cl] complexes should be reassessed in view of the correct MLCT assignments.

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Registry No. *cis*-[Pt(PEt$_3$)$_2$Me$_2$], 22289-34-5; *cis*-[Pt(PEt$_3$)$_2$Et$_2$], 75847-39-1; *cis*-[Pt(PEt$_3$)$_2$Cl$_2$], 15692-07-6; *cis*-[Pt(PEt$_3$)$_2$Br$_2$], 15636-78-9; *cis*-[Pt(PEt$_3$)$_2$(Me)Cl], 22289-46-9; *cis*-[Pt(PEt$_3$)$_2$(Me)Br], 22289-47-0; *trans*-[Pt(PEt$_3$)$_2$(H)Cl], 16842-17-4; *trans*-[Pt(PEt$_3$)$_2$(Me)Cl], 13964-96-0; *trans*-[Pt(PEt$_3$)$_2$(Et)Cl], 54657-72-6; *trans*-[Pt(PEt$_3$)$_2$(H)Br], 18660-33-8; *trans*-[Pt(PEt$_3$)$_2$(Me)Br], 15691-67-5; *trans*-[Pt(PEt$_3$)$_2$(Et)Br], 75847-40-4; *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], 13965-02-1; *trans*-[Pt(PEt$_3$)$_2$Br$_2$], 13985-90-5; *trans*-[Pt(PEt$_3$)$_2$I$_2$], 15636-79-0.

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On the Ligand Field Spectra of Square-Planar Platinum(II) and Palladium(II) Complexes

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The electronic structure of square-planar complexes is apparently characterized by an anomalously low-lying a_{1g} (d_{z^2}) orbital. An attempt is made to describe the situation by using a semiempirical correction parameter σ_{sd}. A number of ligand field spectra of Pt(II) and Pd(II) complexes are analyzed and (re)interpreted on the basis of this procedure. The nature of the σ_{sd} parameter is discussed in terms of second-order perturbation theory.

Introduction

From the point of view of ligand field theory, the electronic structure of square-planar coordination compounds is characterized by a number of unusual features.[1-4] Most of the observed anomalies appear to be related to the energy and the nature of the a_{1g} (d_{z^2}) orbital. The fact that this orbital is apparently situated at much lower energy than can be expected from ligand field considerations is thought to be due to an (n + 1)s–nd mixing phenomenon.[5-11]

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From a number of recent papers, the correction associated with this s–d mixing appears to be very large, and it might be of the same order of magnitude as a typical metal–ligand σ parameter. The most clear-cut case is the $CuCl_4^{2-}$ complex, where an unabiguous assignment of all the relevant transitions has been possible.[4,8] If the angular overlap parameters for the Cu–Cl interaction are denoted by σ and π, the orbital energy differences Δ_i can be expressed as in (1). Here, σ_{sd} is an

$$\begin{aligned} \Delta_1 &= \epsilon(x^2 - y^2) - \epsilon(xy) = 3\sigma - 4\pi \\ \Delta_2 &= \epsilon(x^2 - y^2) - \epsilon(z^2) = 2\sigma + \sigma_{sd} \\ \Delta_3 &= \epsilon(x^2 - y^2) - \epsilon(xz, yz) = 3\sigma - 2\pi \end{aligned} \tag{1}$$

additional parameter which is introduced ad hoc in order to obtain a consistent set of equations; it is supposed to account for the lowering of the d_{z^2} orbital, due to the s–d interaction

$$\epsilon(z^2) = \sigma - \sigma_{sd} \tag{2}$$

From the numerical value of σ_{sd} in the $CuCl_4^{2-}$ case and from a similar analysis of the other square-planar Cu(II) and Ni(II) complexes,[4,8-10] we suggest as the empirical relationship for $3d^n$ systems

$$\sigma_{sd} = \sigma \tag{3}$$

Within the framework of a ligand field model, this means that the stabilizing s–d interaction virtually cancels the destabilizing effects of the square-planar ligand field: the net result is that the orbital energy of d_{z^2} remains virtually unaffected.[12] In a certain sense, the a_{1g} orbital therefore resembles a lone pair on platinum and can be thought of a as a kind of a *gerade* p orbital.[13]

In the past two decades, several very refined spectroscopic measurements have been carried out on square-planar chloro and bromo complexes of Pt(II) and Pd(II). Yet no definitive assignments have been proposed so far, and the spectral interpretation is still controversial.[14-18] It is the purpose of the present paper to reconsider the experimental data very carefully and to attempt a ligand field analysis in the sense of eq 1–3; more specifically we will examine whether or not eq 3 can be extended to 4d and 5d systems.

Spectral Analysis

In a d^8 system with substantial spin–orbit coupling, the three orbital transitions of eq 1 give rise to 12 excited states. Using the Bethe notation for the spin–orbit components, one finds

$$\begin{aligned} &xy \rightarrow x^2 + y^2 \begin{cases} {}^1A_{2g}\text{: } \Gamma_2 \\ {}^3A_{2g}\text{: } \Gamma_1 + \Gamma_5 \end{cases} \\ &z^2 \rightarrow x^2 - y^2 \begin{cases} {}^1B_{1g}\text{: } \Gamma_3 \\ {}^3B_{1g}\text{: } \Gamma_4 + \Gamma_5 \end{cases} \\ &xz, yz \rightarrow x^2 - y^2 \begin{cases} {}^1E_g\text{: } \Gamma_5 \\ {}^3E_g\text{: } \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 \end{cases} \end{aligned} \tag{4}$$

The energy of these states can be calculated from ligand field theory by allowing full configuration interaction within the d^8 manifold;[19,20] the results are a function of the Racah repulsion parameters B and C, the spin–orbit coupling constant ζ, and the orbital energy parameters defined in eq 1.

Table I. Parameter Sets for Various Metal–Ligand Interactions[a,b]

	Pt-Cl	Pt-Br	Pt-NH_3	Pd–Cl	Pd–Br
B	0.060	0.048		0.054	0.053
C	0.240	0.200		0.240	0.220
ζ	0.270	0.250		0.090	0.090
σ	1.242	1.092	1.562	1.015	0.951
π	0.280	0.220	0.170	0.200	0.178

[a] In all cases $\sigma_{sd} = \sigma$. All numerical values in μm^{-1}. [b] For ammonia no separate set of Racah and ζ parameters was derived.

In principle, the experimental spectra can be reproduced by many different sets of numerical parameter values. In practice, of course, the acceptable range is limited severely by the physical meaning of the parameters. Moreover, if there are good reasons to assign one or another of the 12 states unambiguously to one particular spectral band, some of the parameters become interconnected—thus narrowing the possibilities even further. A critical examination of the data on $PtCl_4^{2-}$ and $PtBr_4^{2-}$ leads to the following conclusions.

(i) The only degenerate singlet excited state Γ_5 (${}^1E_g$) can be detected unambiguously from the appearance of an A term in the MCD spectra.[21,22]

(ii) In polarized crystal absorption spectra, only one excited singlet disappears in z polarization, while maintaining its intensity in x,y polarization[1,23-25] A group-theoretical analysis of the vibronic coupling shows that this behavior is only compatible with the transition $xy \rightarrow x^2 - y^2$, Γ_2 (${}^1A_{2g}$).

(iii) The low-intensity triplet band at the low-energy side of Γ_2 (${}^1A_{2g}$) should be assigned to Γ_5 (${}^3B_{1g}$). Indeed, this band is the highest energy triplet band (at 2.43 μm^{-1} in $PtCl_4^{2-}$); it is too close to either ${}^1A_{2g}$ or ${}^1E_g$ (premises i and ii) to be associated with one of the corresponding triplets. Moreover, a vibronic analysis of crystal luminescence spectra of K_2PtCl_4 in a host crystal of Cs_2ZrCl_6 provides rather convicing evidence for the Γ_5 symmetry of the 2.1-μm^{-1} emission.[26,27]

(iv) Several triplet absorptions are observed below the Γ_5 (${}^3B_{1g}$) state. Only one of these, which is strictly x,y polarized, has been assigned:[28] because its polarization behavior is similar to the ${}^1A_{2g}$ state (premise ii), it was thought to correspond to ${}^3A_{2g}$. This particular triplet occurs at about 1.8 μm^{-1} in the chloride complex and 1.7 μm^{-1} in tetrabromoplatinate(II)[17] We believe that the assignment should be reconsidered. Indeed, the polarization of a spin-forbidden transition does not reflect the spatial symmetry of the relevant states; on the contrary, it has the polarization of the spin-allowed transitions, from which intensity is gained by virtue of spin–orbit coupling. Therefore, the x,y-polarized $\Gamma_1 \rightarrow \Gamma_2$ (${}^1A_{2g}$) transition is only able to induce intensity in Γ_2-triplet components. Equation

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(12) Obviously, eq 3 is only a rather crude approximation. From ref 4, for instance, one may calculate $\sigma \approx 0.53$ μm^{-1}, and $\sigma_{sd} \approx 0.63$ μm^{-1}.

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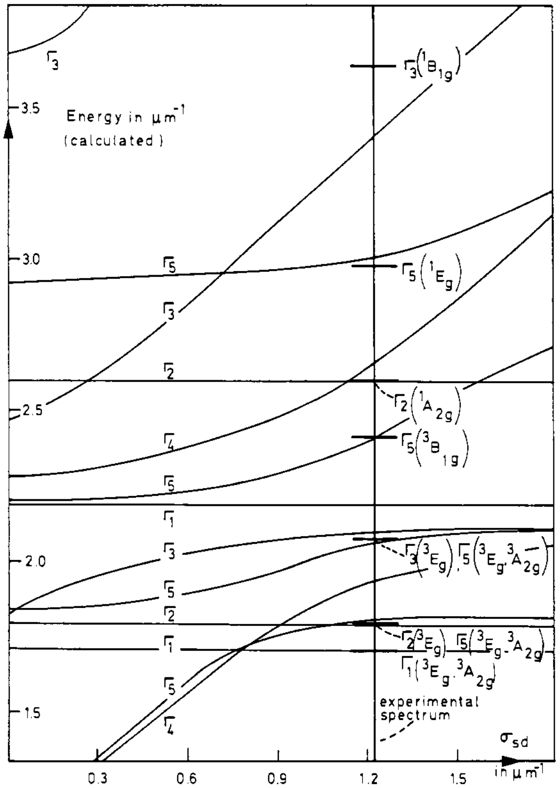

Figure 1. State energy levels of a square-planar d^8 complex, calculated as a function of the parameter σ_{sd}. The other parameters are held constant at the numerical value shown in Table I for $PtCl_4^{2-}$. The experimental levels are shown in heavy lines.

4 shows that the only qualifying triplet is Γ_2 (^3E_g).

(v) The spin-orbit coupling constant of Pd(II), and certainly of Pt(II), is sufficiently large to induce considerable intensity into the spin-forbidden bands. Therefore, it appears very unlikely that any electronic transition could be situated below the spectral origin, where the complexes become completely transparent. This origin was determined by very refined measurements at ~1.66 and 1.55 µm⁻¹ for $PtCl_4^{2-}$ and $PtBr_4^{2-}$, respectively.[25,26]

(vi) As in the case of octahedral compounds, the free-ion values of B, C, and ζ impose an upper limit on the parameters corresponding to a molecular environment (nephelauxetic reduction). From ab initio calculations,[29] one finds for Pt(II) $B = 82.2$ mm⁻¹ and $C = 360.3$ mm⁻¹; from a systematic extrapolation procedure, McClure[30] suggests $\zeta(Pt^{2+}) = 413.5$ mm⁻¹. The spectrum of the Pd^{2+} ion can be rationalized by using[31] $B = 71.3$ mm⁻¹, $C = 317.8$ mm⁻¹, and $\zeta = 116.8$ mm⁻¹.

Assignment of Bands. $PtCl_4^{2-}$ and $PtBr_4^{2-}$. We consider the six conclusions of the previous section as fitting premises with which any parameter set should comply. In order to investigate the position of the a_{1g} (d_{z^2}) orbital, we first optimized all parameters except σ_{sd} by using only those transitions which are not affected by $\epsilon(z^2)$, i.e., Γ_1, Γ_2 (^3E_g), Γ_2 ($^1A_{2g}$), and, to some extent, Γ_5 (^1E_g).

The parameter values are listed in Table I. Then σ_{sd} was varied from 0 to 1.8 µm⁻¹ as shown in Figure 1 for the case of the chloride complex. In the figure the observed levels are compared with the calculated positions. Obviously, poor agreement is obtained for $\sigma_{sd} = 0$, that is, for the unamended ligand field approach. The most satisfactory spectral interpretation results precisely when σ_{sd} is of the order of σ, which means that eq 3 applies. The numerical discription is given in Table II; it is obvious that the thus obtained interpretation is entirely consistent with the six fitting procedures. So far, no detailed calculations had been performed on $PtBr_4^{2-}$, but our results for $PtCl_4^{2-}$ can be compared with the previous works of Martin et al.[14] and of Patterson et al.[26]

Table II. Assignment of the $PtCl_4^{2-}$ and $PtBr_4^{2-}$ Ligand Field Spectra and Comparison of the Observed Spectra with the Energy Levels Calculated from the Parameter Sets Given in Table I[a, b]

	$PtCl_4^{2-}$		$PtBr_4^{2-}$	
state	calcd	obsd[c]	calcd	obsd[d]
Γ_1 (^3E_g, $^3A_{2g}$)	1.713	1.7	1.622	
Γ_2 (^3E_g)	1.799	1.8	1.692	1.70
Γ_5 (^3E_g, $^3A_{2g}$)	1.803	1.8	1.699	1.69
Γ_4 (^3E_g)	[1.941]		[1.804]	
Γ_5 (^3E_g, $^3A_{2g}$)	2.076	2.05	1.940	1.895
Γ_3 (^3E_g)	2.100		1.960	
Γ_1 (^3E_g, $^3A_{2g}$)	[2.189]		[2.064]	
Γ_5 ($^3B_{1g}$)	2.432	2.43	2.235	2.265
Γ_2 ($^1A_{2g}$)	2.597	2.63	2.3975	2.44
Γ_4 ($^3B_{1g}$)	[2.675]		[2.464]	
Γ_5 (^1E_g)	3.016	2.96	2.744	2.71
Γ_3 ($^1B_{1g}$)	3.42	3.65	3.050	3.06

[a] Transitions in brackets are expected to be masked because of their nearly pure singlet → triplet character. [b] All energies are in µm⁻¹. [c] Reference 26; crystal spectrum at 4 K. [d] Reference 25; polarized crystal spectrum at 15 K.

A very weak band at the onset of the spectrum is assigned Γ_1. While this band does indeed correspond to the lowest energy calculated from Table I, both Martin and Patterson calculated triplet levels below the spectral origin.

The next absorption (at 1.8 µm⁻¹ in the chloro and 1.7 µm⁻¹ in the bromo complex) is identified as Γ_2 (^3E_g), consistent with premise iv. As far as we known, this assignment is new. Whereas the intensity-inducing singlet Γ_2 ($^1A_{2g}$) is completely quenched in z polarization,[23,25,28] the Γ_2 triplet is not: it exhibits some observable remaining intensity. This suggests the presence of still another triplet, which is of course compatible with the fact that we calculate a Γ_5 (^3E_g, $^3A_{2g}$) at virtually the same energy as Γ_2 (^3E_g).

The three Γ_5 states, which are predicted in the triplet region, are of $^3A_{2g}$, ^3E_g, and $^3B_{1g}$ parentage. A measure for their singlet admixture might be found from the average value $\{S(S+1)\}$, which can easily be calculated from their wave functions. Their singlet character and hence their absorption intensity are predicted to increase the nearer they are to Γ_5 (^1E_g). This corresponds to the observed extinction coefficients Γ_5 ($^3B_{1g}$) being the most intense spin-forbidden band with $\epsilon \approx 12$ cm⁻¹ M¹ for $PtCl_4^{2-}$.[23]

The Γ_4 (^3E_g, $^3B_{1g}$) level which is expected to be found between the two lowest Γ_5 triplet components might not be observable, since no low-lying Γ_4 singlets are available, wherefrom this triplet might borrow intensity; its $\{S(S+1)\}$ value is quite close to 2. At 2.05 µm⁻¹ in $PtCl_4^{-}$[23,28] and ~1.9 µm⁻¹ in $PtBr_4^{2-}$,[25] a broad band is found, which is matched very well by the two triplet components Γ_5 (^3E_g) and Γ_3 (^3E_g). The close-lying Γ_1 band is probably of lower intensity than any of the neighboring transitions, again due to the absence of an intensity-giving Γ_1 singlet.

The exact position of Γ_5 ($^3B_{1g}$) is of prime importance in order to test the validity of eq 3. Indeed, from Figure 1, it is clear that the position of this triplet is very sensitive to σ_{sd} and $\epsilon(z^2)$. It is mixed to a singnificant extent with Γ_5 (^1E_g), thereby acquiring a rather high intensity; its position is calculated at the low-energy side of Γ_2 ($^1A_{2g}$), as required by premise iii.

The position of Γ_5 (^1E_g) on the other hand imposes an upper limit on the energy of the a_{1g} (d_{z^2}) orbital. Increasing σ_{sd} would

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Table III. Assignment of the $PdCl_4^{2-}$ and $PdBr_4^{2-}$ Ligand Field Spectra and Comparison of the Observed and Calculated Energy Levels[a, b]

	$PdCl_4^{2-}$		$PdBr_4^{2-}$	
state	calcd	obsd	calcd	obsd
Γ_5 ($^3B_{1g}$)	1.786	1.770	1.666	1.696
Γ_2 ($^1A_{2g}$)	2.114	2.170	2.023	2.020
Γ_5 (^1E_g)	2.341	2.320	2.210	2.19
Γ_3 ($^1B_{1g}$)	2.679	2.890[c]	2.507	2.699

[a] The observed energy levels are taken from ref 32 and refer to polarized crystal spectra at 15 K; the calculated values were obtained by means of the parameters shown in Table I. [b] Energies are in μm^{-1}. [c] Harrison et al.[33] have found a band at 2.89 μm^{-1}, which is not reported by Martin et al.[32]

cary the Γ_5 (^1E_g) state to higher energy, mainly because of its strong interaction with Γ_5 ($^3B_{1g}$).

Finally, the band series is terminated on Γ_3 ($^1B_{1g}$) in the near-UV region. An earlier proposal[14] that this band would overlap with Γ_5 (^1E_g) cannot be confirmed by our calculations: from Figure 1 it can be seen that such an overlap would occur for $\sigma_{sd} \approx {}^1/_2\sigma$. However, this would at the same time induce a shift of the three Γ_5 triplets to the red side of the spectrum, thereby destroying much of the agreement between theory and experiment.

$PdCl_4^{2-}$ and $PdBr_4^{2-}$. The spectra of the palladium halides are formally identical with those of their platinum analogues, except for a strongly reduced intensity of the triplet absorption, due to a lower ζ value.[32,33] With an analysis of the same type as described in the previous section, the parameters of Table I were derived for $PdCl_4^{2-}$ and $PdBr_4^{2-}$.

A comparison of theory and experiment—together with the proposed assignment—is given in Table III. Only the most intense singlet–triplet transition $\Gamma_1 \rightarrow \Gamma_5$ ($^3B_{1g}$) is very observable.

In previous work,[32] it was not possible to identify bands that might be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ or $^1A_{1g} \rightarrow {}^3B_{1g}$ transitions.

$Pt(NH_3)Cl_3^-$. The spectra of most other Pt(II) and Pd(II) complexes were recorded on solutions and are characterized by a lower resolution.[15,34] A remarkable exception is the spectrum of crystalline yellow Cossa's salt $KPt(NH_3)Cl_3{\cdot}H_2O$, which was studied independently in two detailed reports.[35,36] Francke and Moncuit[35] started from the assumption that the π parameter for NH_3 should be equal to zero. This is a quite reasonable assumption in octahedral complexes,[37] where π-($M-NH_3$) serves as a reference value, with respect to which all other ligand field parameters are defined. However, in square-planar complexes, an independent evaluation of all parameters becomes possible, and there is no a priori reason to exclude any π contribution from NH_3.

Therefore, we preferred to proceed on a different basis, by taking B, C, ζ, σ, and π for Pt–Cl from Table I, thus assuming the transferability of these parameters from $PtCl_4^{2-}$ to $Pt(NH_3)Cl_3^-$. In addition to this, we used the well-known[2] linear relationship between the first singlet absorption ($xy \rightarrow x^2 - y^2$) of a given complex and the number of NH_3 ligands. This means, that in the series $Pt(NH_3)_nCl_{4-n}^{n-2}$, where n runs from 0 to 4, one has

$$\Delta E(xy \rightarrow x^2 - y^2) = E(^1A_{2g}, PtCl_4^{2-}) + (n/4)[10Dq(NH_3) - 10Dq(Cl^-)] \quad (5)$$

Table IV. Calculated[a] and Observed[b] Band Positions of $KPt(NH_3)Cl_3{\cdot}H_2O$[c, d]

state	orbital transition	calcd state position	obsd band position (polarizn)
$^1B_2$	$xy \rightarrow x^2 - y^2$	2.932	2.94 (x)
$^1A_2$	$xz \rightarrow x^2 - y^2$	3.257	3.25 (weak)
$^1B_1$	$yz \rightarrow x^2 - y^2$	3.345	3.37 (z)
$^1A_1$	$z^2 \rightarrow x^2 - y^2$	4.360	

[a] From Table I. [b] Polarized crystal spectra[36] at 15 K. [c] Symmetry labels refer to C_{2v} (y) point group: the amine is placed on the y axis. The triplets are discussed in the text. [d] All energies are in μm^{-1}.

Table V. Ligand Field Parameters (μm^{-1}) for $PtCl_4^{2-}$

	TG[a]	this work	free ion
B	0.033	0.060	0.082
C	0.056	0.240	0.360
ζ	0.136	0.270	0.414
σ	1.151	1.242	
π	0.213	0.280	
σ_{sd}	0.0	1.242	

[a] Reference 17; the Tuszynski–Gliemann treatment.

The data for chloro(amino)platinates(II) can be found in the literature;[2,35,36,38–40] recently the $^1A_{2g}$ absorption of $Pt(NH_3)_4^{2+}$ has been assigned in a single crystal.[41] From these data and eq 5, the spectrochemical strength of NH_3 can be estimated at $10Dq(NH_3) = 4.006$ μm^{-1}.

Finally, eq 3 was extended to the low-symmetry case under consideration by putting σ_{sd} equal to the average σ value: $\sigma_{sd} = (1/4)[3\sigma(Pt-Cl) + \sigma(Pt-NH_3)] = \bar{\sigma}(Pt-L)$. This leaves only one independent parameter in the fitting process, namely, the ratio $\pi(Pt-NH_3)/\sigma(Pt-NH_3)$. A consistent spectral interpretation can readily be obtained for $\pi/\sigma \approx 0.11$. The resulting amine parameters are included in Table I, and a comparison between observed and predicted band positions can be found in Table IV.

At 2.10 μm^{-1} an x-polarized singlet–triplet absorption is observed, indicating a B_2-triplet component, which is strongly coupled to the x-polarized $^1B_2$ (the 2.94 μm^{-1} transition of Table IV). Obviously, this phenomenon is the low-symmetry analogue of premise iv; the numerical calculations do indeed predict a B_2-triplet component with significant singlet admixture at 2.065 μm^{-1}.

In the neighborhood of 2.3 μm^{-1}, we calculate several closely spaced triplet components with sufficient singlet admixture so as to be observable. Although a broad triplet band is found in the experimental spectrum at precisely this wavenumber, no detailed resolution of the band has been carried out so far.

The Tuszynski–Gliemann (TG) Treatment. It is interesting to compare our assignments to the recent work of Tuszynski and Gliemann.[17] These authors carried out a classical crystal field analysis, which amounts to letting $\sigma_{sd} = 0$. On this basis, one finds the highest occupied orbital to be d_{z^2}.

The first moderately intense band—for $PtCl_4^{2-}$ at 2.1 μm^{-1} and characterized by $f \approx 10^{-4}$—is then assigned to the singlet–singlet excitation $x^2 - y^2 \leftarrow z^2$ ($^1B_{1g}$). In the present work, this same band is assigned as a singlet–triplet absorption, its intensity is in the borderline region between spin-allowed and spin-forbidden transitions. The basic reason that the triplet hypothesis is preferable is that the TG assignment leads to

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unacceptable parameters. Indeed, if the 2.1-μm^{-1} band is $^1B_{1g} \leftarrow {}^1A_{1g}$, the $^3B_{1g} \leftarrow {}^1A_{1g}$ band must be positioned even lower, that is, at $\sim$1.7 μm^{-1} (which is what Gliemann does), but this means that the parameters ζ and B, C (or F_2, F_4) must be reduced so drastically that the ligand field picture cannot reasonably be maintained. For $PtCl_4^{2-}$, we recalculated the TG parameters in our notation, and we find the values shown in Table V.

As for the other bands, it is remarkable that the TG assignments satisfy most of our fitting premises: only for (iii) and (iv) is there a definite lack of agreement. The Γ_5 absorption (at 2.43 μm^{-1} in $PtCl_4^{2-}$) is assigned as $^3B_{1g}$ by us and as $^3A_{2g}$ by Gliemann. Yet the corresponding singlet $^1A_{2g}$ is only 0.2 μm^{-1} higher (at 2.63 μm^{-1})—an impossibly small energy gap.

The x,y-polarized band at 1.8 μm^{-1} for $PtCl_4^{2-}$ and 1.7 μm^{-1} for $PtBr_4^{2-}$ has been assigned Γ_2 (^3E_g) by us and Γ_4 ($^3B_{1g}$) by Gliemann. The proximity of the intensity-giving Γ_2 ($^1A_{2g}$) seems to favor the Γ_2 hypothesis; the Γ_4 state is calculated to be nearly purely triplet in nature.

Concluding Remarks

(i) For a number of square-planar Pt(II) and Pd(II) complexes, we have proposed spectral assignments that appear to be compatible with all the available experimental data. We have shown that the relatively complicated pattern of d^8 states can be rationalized by a simple orbital model, provided we introduce an additional parameter σ_{sd}. This parameter determines the energy of the a_{1g} (d_{z^2}) orbital; its numerical value can be adequately described by eq 3 or by the low-symmetry extension $\sigma_{sd} = \bar{\sigma}$, where $\bar{\sigma}$ is the average σ parameter for the four ligands.

(ii) The numerical value of the correction parameter σ_{sd} is admittedly very large. Yet, apart from the subsequent agreement between theory and spectra, additional confidence in eq 3 can be derived from the very reasonable values of the *other* ligand field parameters, which are of course intimately connected to the value of σ_{sd}. For instance, from Table I, one can calculate the values of $10Dq = 3\sigma - 4\pi$ for the different Pt(II) complexes. For Br$^-$, Cl$^-$, and NH_3, one finds 2.396, 2.606, and 4.006 μm^{-1} respectively.

The corresponding 10Dq values for Cr(III) complexes[37] are 1.230, 1.322, and 2.125 μm^{-1}. It is gratifying to find that the ratio of the 10Dq values for one given ligand is nearly constant in the three cases. Jørgensen had observed a constant 10Dq ratio upon variation of the metal ion within a series of octahedral complexes.[42] The present results tend to point to a generalization of this empirical rule by including the square-planar complexes as well.

(iii) It is not difficult to understand why the σ_{sd} parameter is especially important in square-planar complexes. Indeed, in the cubic groups, T_d and O_h, nd_{z^2} and $(n + 1)$s belong to different irreducible representations; they cannot interact under the influence of the ligands. Even in distorted or substituted tetrahedrons or octahedrons, the matrix element for interaction will remain small.

The four most important geometries where the mixing of nd_{z^2} and $(n + 1)$s becomes important are the square plane D_{4h}, the linear $D_{\infty h}$ molecule, the square pyramid C_{4v}, and the trigonal bipyramid D_{3h}. In these four cases $(s|V|z^2)$ can in principle give rise to a more or less important depression of $\epsilon(z^2)$. Within the framework of second-order perturbation theory, this depression is given by

$$\sigma_{sd} = [(s|V|z^2)]^2/(E^\circ{}_s - E^\circ{}_d) \qquad (6)$$

The interaction element can be written as a function of one single matrix element for the four cases:

$$(s|V(D_{4h})|z^2) = -2(s|V_z|z^2)$$

$$(s|V(D_{\infty h})|z^2) = 2(s|V_z|z^2)$$

$$(s|V(C_{4v})|z^2) = -(s|V_z|z^2)$$

$$(s|V(D_{3h})|z^2) = \tfrac{1}{2}(s|V_z|z^2)$$

where V_z is the ligand field Hamiltonian associated with one single ligand on the z axis. This means that the σ_{sd} corrections should be in the ratio 16:16:4:1 for the four geometries under consideration. Therefore simple perturbation arguments seem to justify the neglect of s–d mixing in all cases except square planes and linear molecules.

Registry No. $PtCl_4^{2-}$, 13965-91-8; $PtBr_4^{2-}$, 14493-01-7; $PdCl_4^{2-}$, 14349-67-8; $PdBr_4^{2-}$, 14127-70-9; $KPt(NH_3)Cl_3$, 13820-91-2.

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