

Electronic Absorption Spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ in Tetrahydrofuran

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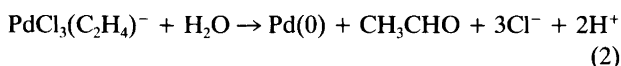
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The dinuclear complex $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ dissolved in dry tetrahydrofuran (THF) saturated with ethene has been titrated with $\text{LiCl}(\text{THF})$ according to the reaction



and the absorption spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ in the UV/VIS spectral range has been measured. The charge-transfer bands have been assigned in accordance with a published assignment of the bands in the spectrum of the analogous Pt complex in aqueous solution, as singlet–singlet transitions from the metal d-levels to the ethene- π^* level. A strong band in the UV range has been tentatively assigned as an ethene- π to a metal-d transition. The spectrum of the analogous Pt complex has also been measured in THF. The earlier measured spectrum of the Pt complex in aqueous solution has been checked and extended to higher transition energies and an alternative assignment for these bands, viz. as singlet–triplet d to π^* transitions, is discussed. That they should be differently assigned from those of the Pd complex is likely, since the magnetic circular dichroism spectra of the two complexes differ.

In this paper the UV/VIS spectra in dry tetrahydrofuran (THF) of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$, trichloro(ethene)palladate(II), and its corresponding platinum(II) analogue are reported. The suggested assignments of the absorption bands of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ are based on a comparison with a published¹ assignment of the electronic absorption spectrum of the corresponding platinum(II) complex $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$, Zeise's anion, in aqueous solution. The spectra of the two mononuclear complexes are qualitatively similar, with the bands of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ shifted to higher transition energies than those of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ (cf. Figs. 3 and 4 later). It is not possible to make any measurements on the palladium complex in aqueous solution, because it undergoes rapid redox reactions according to the well-known Wacker process, reaction (2).



Following the industrial development of this process in the 1950's, experimental² and theoretical³ studies of Pd-assisted nucleophilic additions to olefins have increased enormously. The Wacker process has been the subject of many kinetic and equilibrium studies, and there seems to be general agreement as to the reaction mechanism.⁴ Despite the importance of the process, no published electronic absorption spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ has appeared.

$\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ has been prepared by addition of $\text{LiCl}(\text{THF})$ to the dinuclear complex $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ (Kharasch's compound) dissolved in dry THF, according to reaction (3).



The experiments reported here show that it is possible to prepare stable solutions with $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ in dry THF, if the temperature is kept below 0°C and the solution is saturated with ethene: the redox reaction (2) is suppressed and there is no formation of PdCl_4^{2-} according to the reverse of reaction (1), except when the chloride concentration is in very large excess over that of palladium(II).

For comparison, the absorption spectrum of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ [prepared according to the analogue of reaction (3)] has also been measured in THF. The aqueous absorption spectrum¹ of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ has been extended to 190 nm (5.26 μm^{-1}).

The assignment is based on the reasonable assumption that $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ has the same structure as $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$, i.e. C_{2v} symmetry.⁵ No structural information seems to be available concerning $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$, but the structure of the dinuclear complex $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ is known;⁶ it belongs to the symmetry group C_{2h} . The structure is similar to that of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in the sense that the C=C double bond is perpendicular to the plane spanned by the metal and chlorine atoms, cf. Fig. 5 later.

Experimental

Chemicals. $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ and $\text{Pt}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ were prepared according to the methods of Kharasch⁷ and Chatt,⁸ respec-

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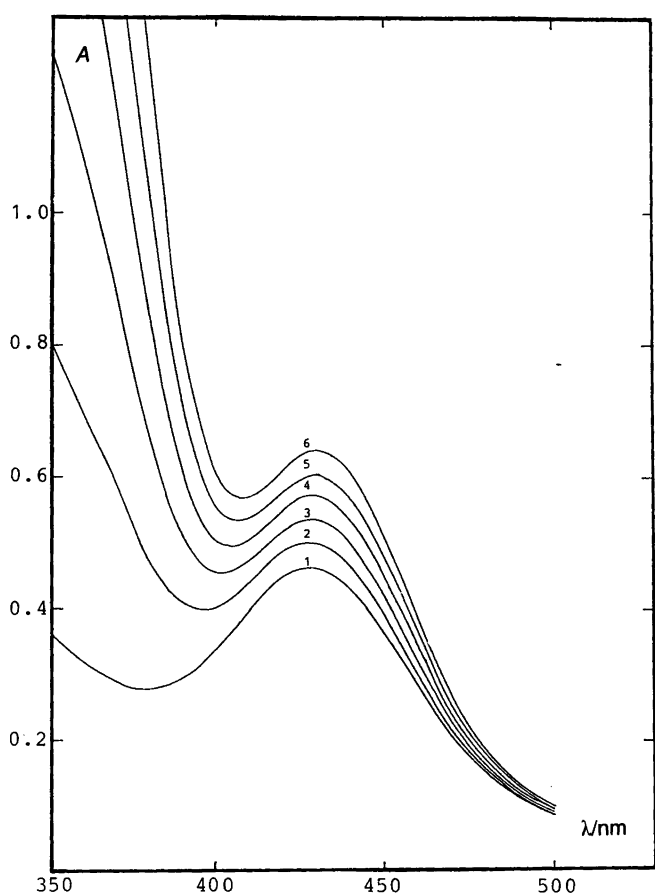


Fig. 1. Spectrophotometric titration curves according to reaction (3): (1) no Cl^- added; (2) 0.2 Cl^-/Pd added; (3) 0.4 Cl^-/Pd ; (4) 0.6 Cl^-/Pd ; (5) 0.8 Cl^-/Pd ; (6) 1.0 Cl^-/Pd . The spectrum corresponding to 1.2 Cl^-/Pd coincides with (6).

tively. Found: C 12.2; H 1.86; Cl 34.5. Calc. for $\text{C}_4\text{H}_8\text{Cl}_4\text{Pd}_2$: C 11.7; H 1.96; Cl 34.5. Tetrahydrofuran (Merck p.a.) was distilled once prior to use. Ethene was of analytical grade (Alfax, N 35).

Apparatus. Low-temperature (-20°C) spectra were recorded with a closed-flow thermostatted titration vessel, previously described,⁹ attached to a Cary 2200 UV/VIS spectrophotometer. A spectrum at liquid-nitrogen temperature was measured with a Milton Roy Spectronic 1201 single-beam spectrophotometer and with a path length of 10 mm. Magnetic circular dichroism (MCD) spectra were recorded with an apparatus described elsewhere.¹⁰

Procedure. The dinuclear complex was dissolved in ethene-saturated, freshly distilled THF, in concentrations up to 6 mM. Both complexes dissolved within a few minutes. To the titration vessel was added a known volume (ca. 50 ml) of ethene-saturated THF, the temperature was lowered to -20°C and a baseline recorded between 600 nm and solvent cutoff (ca. 210 nm). A known volume of the solution containing the complex was then transferred to the titration vessel. The vessel was continuously flushed with ethene in order to keep the solution saturated and to exclude humid air.

The dinuclear complex was titrated with LiCl (typically

0.1 M) in dry, ethene-saturated THF, according to reaction (3), see Fig. 1. The titration was measured spectrophotometrically to determine how much chloride is needed to break the chloride bridge, and if substitution to PdCl_4^{2-} , according to the reverse of reaction (1), occurs. Cl^- was added in 0.1 equivalent portions up to the equivalence point (e.p. Cl^-/Pd 1:1). After e.p. the additions had to be larger in order to observe any spectral changes.

The absorption spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ was also measured at liquid-nitrogen temperature. The solvent was a mixture of THF and diethylether (3:7 v/v) saturated with ethene. The spectrum is identical with that in THF, i.e. no more bands appear to be present than those displayed later in Fig. 3.

The aqueous spectrum of Zeise's anion over the range 250–190 nm was recorded in 30 mM aqueous HCl at 25°C . Chatt and Leden¹¹ determined the equilibrium constant for reaction (4) as $K = 3$ mM. This means that 91 % of the total Pt concentration is present as $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ at the chloride concentration used. It has to be low to minimize the absorption of Cl^- , which is quite large below 200 nm. The spectrum agrees with that previously published.¹

As quoted in the introductory section, the spectra of the two mononuclear complexes are qualitatively similar, which indicates identical assignments. To obtain additional spectral information, the MCD spectra were measured at

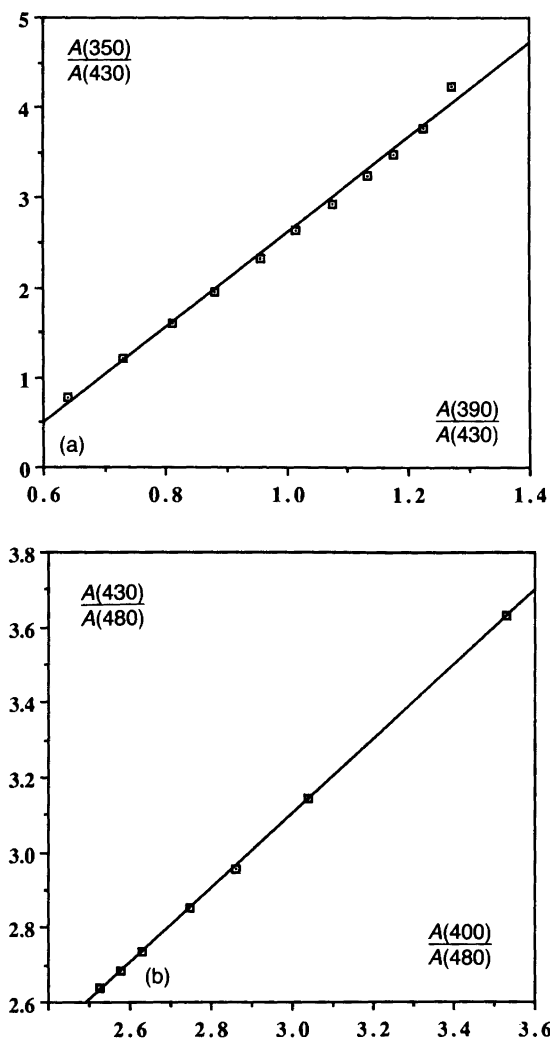
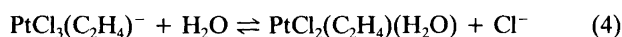


Fig. 2. Absorption ratio plots according to Coleman *et al.*¹² Concentration ratio Cl^-/Pd : (a) $0 \leq \text{Cl}^-/\text{Pd} \leq 1$; (b) $1 \leq \text{Cl}^-/\text{Pd} \leq 27$. Wavelengths are chosen to give maximum absorbance changes.

room temperature, with 3 mM concentrations of complexes dissolved in ethene-saturated THF. The spectra are displayed later in Figs. 3 and 4.



Results and discussion

Number of absorbing species. The Coleman plots¹² in Fig. 2(a) indicate that there are only two absorbing species present before e.p. (i.e. $\text{Cl}^-/\text{Pd} < 1:1$), probably $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ and $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$. (Corresponding plots for the Pt-complexes give analogous results.) Even though the solid compound $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ possibly retains its stoichiometry in solution, which the corresponding platinum complex does,¹³ it cannot be excluded that it dissociates upon dissolution to form $\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{THF})$. Since there is only one species present before addition of LiCl and two after, there is no equilibrium between $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$ and

the hypothetical $\text{PdCl}_2(\text{C}_2\text{H}_4)(\text{THF})$; it must be one of the two that reacts with Cl^- and forms $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$. Also after e.p. there are two species present, $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ and PdCl_4^{2-} , although the latter occurs in very small amounts, even at a large excess of Cl^- . To increase the yield of PdCl_4^{2-} , the concentration of free ethene in solution must be decreased by flushing the solution with nitrogen. (A positive identification of PdCl_4^{2-} in THF is possible, because its spectrum is very similar to that in aqueous solution.¹⁴) The titrations show that $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ can be prepared in THF at -20°C in almost 100% yield by adding stoichiometric amounts of Cl^- to $\text{Pd}_2\text{Cl}_4(\text{C}_2\text{H}_4)_2$.

Number of bands. Spectra of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ were recorded over the concentration interval 10^{-4} – 6×10^{-3} M, without any significant difference. A Gaussian analysis was performed on the spectrum, using absorptivity values every 2 nm. The results are presented in Tables 1–3, together with

Table 1. Spectral data for $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ in tetrahydrofuran.

$\bar{\nu}/\mu\text{m}^{-1}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\Delta\bar{\nu}_{1/2}/\mu\text{m}^{-1}$	Proposed assignments (cf. Tables 4 and 5)	
		Orbital	State	
1.95	10	0.38	singlet–triplet d–d	
2.31	265	0.32	singlet–singlet d–d	
2.81	1140	0.38	$yz \rightarrow \pi^*$	$^1\text{A}_1 \rightarrow ^1\text{B}_2$
3.28	3100	0.46	$z^2 \rightarrow \pi^*$	$^1\text{B}_1$
3.81	4900	0.34	$xz \rightarrow \pi^*$	$^1\text{A}_1$
4.15	29100	0.36	$\pi \rightarrow x^2 - y^2$	$^1\text{A}_1$
4.91	42000 ^a		$\pi \rightarrow \pi^*$?	

^aEstimated from absorptivity data $\leq 4.67 \mu\text{m}^{-1}$.

Table 2. Spectral data for $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in tetrahydrofuran.

$\bar{\nu}/\mu\text{m}^{-1}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\Delta\bar{\nu}_{1/2}/\mu\text{m}^{-1}$	Proposed orbital assignments
2.60	87	0.34	d–d
2.93	480	0.32	d–d?
3.25	1560	0.32	} d→π*
3.75	5060	0.42	
4.11	4130	0.36	

Table 3. Spectral data for $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in aqueous solution and crystal.¹⁵

$\bar{\nu}/\mu\text{m}^{-1}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	$\Delta\bar{\nu}_{1/2}/\mu\text{m}^{-1}$	Crystal ¹⁵ $\bar{\nu}/\mu\text{m}^{-1}$	Proposed orbital assignments
3.0	250		3.03	d–d
			3.12	
			3.41	
3.44	750	0.29	3.46	singlet–triplet d–π*
3.77	1360	0.30	3.57	
4.16	3220	0.45		
5.21	35000			singlet–singlet d–π*

Table 4. Section rules in the C_{2v} point group.

Transition	Selection rule
${}^1A_1 \rightarrow {}^1A_1$	Electric-dipole allowed
${}^1A_1 \rightarrow {}^1A_2$	Electric-dipole forbidden
${}^1A_1 \rightarrow {}^1B_1$	Electric-dipole allowed
${}^1A_1 \rightarrow {}^1B_2$	Electric-dipole allowed

suggested assignments (see also Table 4). The experimental spectra, together with the Gaussian bands, are displayed in Figs. 3 and 4. Below $2.5 \mu\text{m}^{-1}$ there are two weak bands ($\epsilon_{\text{max}} < 300 \text{ M}^{-1} \text{ cm}^{-1}$), between 2.5 and $4.0 \mu\text{m}^{-1}$ three symmetry-allowed bands ($1000 < \epsilon_{\text{max}} < 5000 \text{ M}^{-1} \text{ cm}^{-1}$) and above $4 \mu\text{m}^{-1}$ two symmetry-allowed and extremely strong bands ($\epsilon_{\text{max}} > 25000 \text{ M}^{-1} \text{ cm}^{-1}$). In the case of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in THF (Table 2) the pattern is similar, but there are no extremely strong bands present in the investigated spectral region. The bands of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ are shifted about $0.4 \mu\text{m}^{-1}$ to higher transition energies than

those of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$. One extremely strong band above $5 \mu\text{m}^{-1}$ is found in the aqueous solution spectrum of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ (Table 3).

The solubility of LiCl in THF was determined as 1.1 M at room temperature. A 0.15 M solution was cooled to -80°C without precipitation of LiCl.

Group-theoretical analysis. Both $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ and $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ belong to the C_{2v} point group. The coordinate system is shown in Fig. 5 and is the same as that used for $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ by Denning *et al.*¹ (but changed to a right-handed system) and by Chang and Zink.¹⁵

The selection rules in the C_{2v} point group are summarized in Table 4. The electronic ground state has the symmetry 1A_1 . The electric-dipole-forbidden transition may gain some intensity by vibronic coupling. Such transitions may be seen in the spectrum as weak bands.

Concerning the orbitals involved, Hartley *et al.*¹ concluded that only the metal d and ethene π and π^* orbitals were relevant for a discussion of the transitions (referred to as d-to- π^*) corresponding to the observed absorption

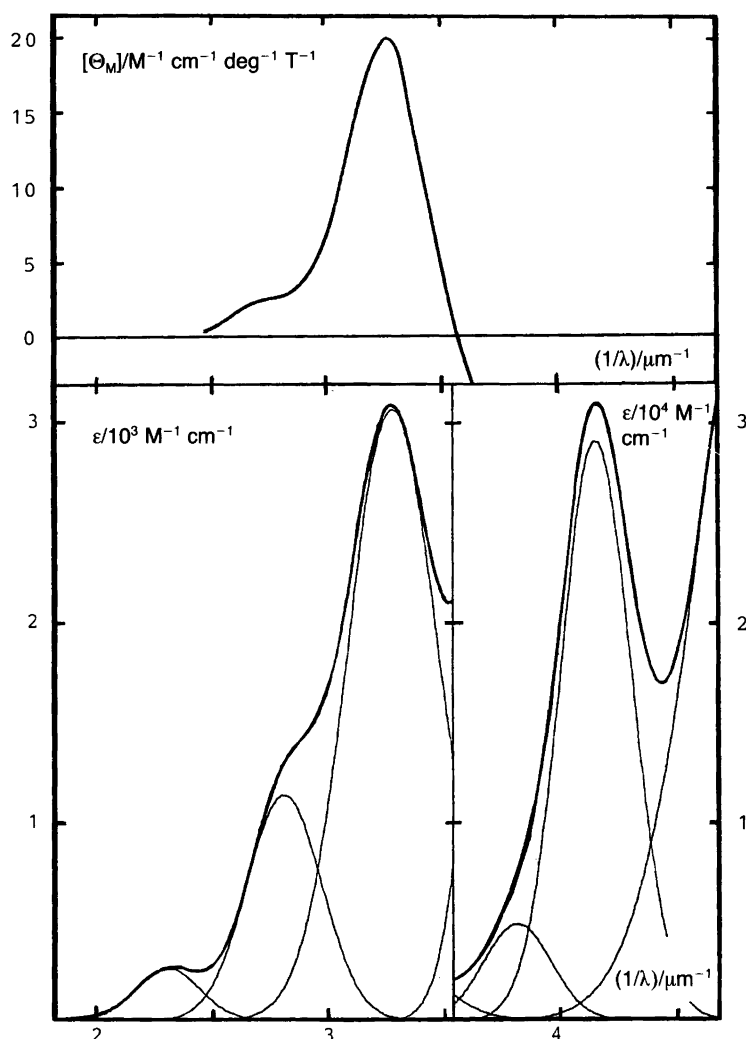


Fig. 3. Absorption spectrum and calculated Gaussian curves (lower part) and the magnetic circular dichroism spectrum (upper part) of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ in THF.

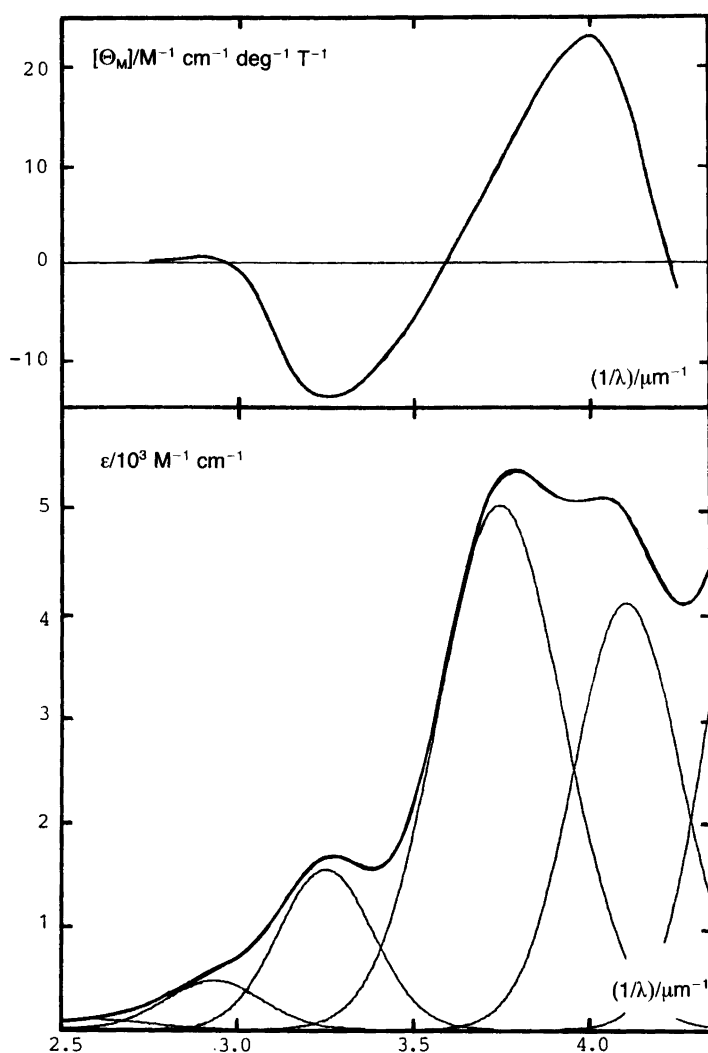


Fig. 4. Absorption spectrum and calculated Gaussian curves (lower part) and the magnetic circular dichroism spectrum (upper part) of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in THF.

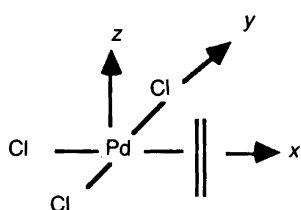


Fig. 5. The coordinate system, with the x axis through the ethene(II) ligand (i.e. parallel with the twofold symmetry axis), the z axis perpendicular to the molecular plane and the y axis perpendicular to the page.

Table 5. Symmetry classification of the orbitals and the electric-dipole transitions.

Orbitals	Symmetry species	Orbital transitions (symmetry allowed except where noted)	
$x^2 - y^2$	a_1	$xy \rightarrow x^2 - y^2$	$(xy \rightarrow \pi^*$ forbidden)
xy	b_2	$xz \rightarrow x^2 - y^2$	$xz \rightarrow \pi^*$
xz	b_1	$(yz \rightarrow x^2 - y^2$	$yz \rightarrow \pi^*$
yz	a_2	forbidden)	
z^2	a_1	$z^2 \rightarrow x^2 - y^2$	$z^2 \rightarrow \pi^*$
π	a_1	$\pi \rightarrow x^2 - y^2$	$\pi \rightarrow \pi^*$
π^*	b_1		

bands of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in the UV/VIS spectral region between 3.1 and 4.5 μm^{-1} . That conclusion followed from a consideration of the ionization potentials of platinum and ethene. The same arguments obviously also apply in the case of palladium, and it is reasonable to expect that the ionization potential of a valence d orbital is equal to or

slightly smaller here than in platinum. This follows from the values of the first and second potentials¹⁶ [$\text{M}(\text{g}) \rightarrow \text{M}^+(\text{g}) + e^-$, 8.3 eV for $\text{M} = \text{Pd}$ and 9.0 eV for $\text{M} = \text{Pt}$, the second ones are 19.46 (Pd) and 18.56 (Pt) eV], and that the effective charge of both metal atoms in a square-planar complex is less than one unit. [Folkesson and Larsson¹⁷

reported $q_{\text{eff}} = (0.4 \pm 0.2)e^-$, where e is the electronic charge, in the tetrachloro complexes.]

The symmetry species of the relevant orbitals and the electric-dipole-allowed transitions to the empty x^2-y^2 and π^* orbitals are summarized in Table 5: there are three allowed $d(yz, z^2, xz)$ -to- π^* transitions and one forbidden. The one-electron energy-level diagram and the transitions are schematically displayed in Fig. 6.

Assignments. The only published UV spectrum of PtCl₃(C₂H₄)⁻ is that by Hartley *et al.*,¹ who investigated the interval from 1.5 to 4.5 μm^{-1} in the aqueous-solution spectrum of Zeise's anion. Chang and Zink¹⁵ have studied the single-crystal spectrum in the region below 3.7 μm^{-1} , which contains the d-d transitions and the first d→ π^* transition. Hartley *et al.*¹ suggested, from a comparison with other Pt-complexes (and from the ionization potentials) that the three bands at 3.44, 3.77 and 4.16 μm^{-1} (cf. Table 3) are probably due to allowed d→ π^* transitions. The band(s) at 3.0 μm^{-1} are assigned as one or more d-d transitions. By substituting the ligand in the *trans* position to the olefin, and changing the solvent, the following d-orbital energy ordering was suggested:¹ $x^2-y^2 \gg xy > z^2 > yz > xz$. Chang and Zink¹⁵ also give the same order, except for the z^2 orbital, which they omit completely in their report. However, that orbital is obviously important in this context, since the transition $z^2 \rightarrow \pi^*$ is one of the three allowed d→ π^* transitions. A comparison with the spectrum¹⁴ of the structurally identical complex PtCl₃(H₂O)⁻, i.e. C_{2v}, further supports the assignment by Hartley *et al.*¹ The d-d spectrum of the latter shows bands at nearly the same transition energies (ca. 3 μm^{-1}) as PtCl₃(C₂H₄)⁻. In PtCl₃(H₂O)⁻ there is, however, no absorption at higher wavenumbers until a maximum around 4.3 μm^{-1} , i.e. at higher energy than in Zeise's anion. The most reasonable explanation is that the presence of ethene adds a new, empty orbital

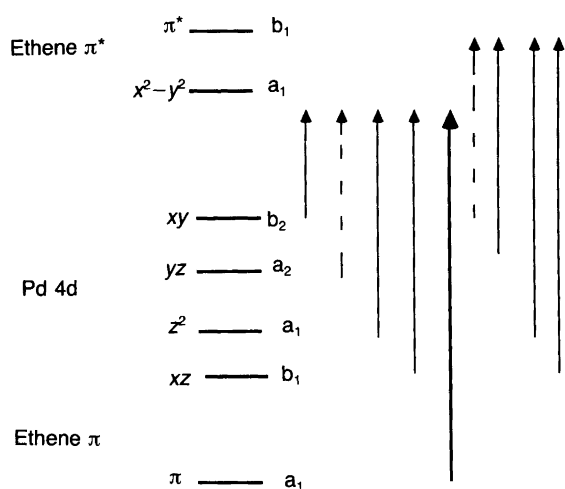


Fig. 6. Schematic molecular orbital diagram. The Cl 3s and 3p orbitals have been excluded. Dashed lines indicate dipole-forbidden transitions. Those two shown are vibronically allowed.

(i.e. π^*) to the complex, with an energy higher than x^2-y^2 , and that the actual transitions are allowed (filled-d)-to-(empty- π^*). Chang and Zink¹⁵ assign the corresponding bands in the crystal spectrum of PtCl₃(C₂H₄)⁻ (labelled D and E) as singlet-triplet d→ π^* transitions, and that assignment is retained in this paper.

Concerning the extremely strong band in the aqueous spectrum around 5.2 μm^{-1} with $\epsilon_{\text{max}} \approx 3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, cf. Table 3, there is no corresponding band in PtCl₃(H₂O)⁻; this suggests that it may be assigned as the ethene- π -to-metal-d(x^2-y^2) transition, or alternatively as a singlet-singlet d→ π^* transition (*vide infra*).

It is obviously possible to transfer these orbital assignments to the spectrum of PdCl₃(C₂H₄)⁻ (cf. Table 1). The d-d transitions cannot be seen as separate bands in the spectrum, but the spin-allowed ones can probably all be found in the band at 2.31 μm^{-1} , while the spin-forbidden transitions make up the weak band at 1.95 μm^{-1} . Both the transition energies and the molar absorptivities are close to those of the d-d bands of the isostructural aqua complex,¹⁴ PdCl₃(H₂O). The next three bands at higher wavenumbers (2.5–4.0 μm^{-1} , $1000 < \epsilon_{\text{max}} < 5000 \text{ M}^{-1} \text{ cm}^{-1}$) can unambiguously be assigned as the three allowed, singlet-singlet $d(yz, z^2, xz) \rightarrow \pi^*$ transitions. The interpretation is consistent with the existence of the MCD spectrum. Because the symmetry is low (C_{2v}) and the complex is diamagnetic, there can only exist a so-called MCD B-term.¹⁸ Two electronic states can contribute to such a term if they can mix via the magnetic dipole vector. States with a small energy difference will contribute more than those with a large one [eqn. (33) of Ref. 18, $B(a \rightarrow j)$]. Concerning the B-term in this spectral region (2.5–4.0 μm^{-1}), it is thus only necessary to consider those states which arise from the $d\pi^*$ configurations, since they have the lowest energy differences. The application of eqn. (33) of Ref. 18 [$B(a \rightarrow j)$], shows that the $d(yz, z^2, xz), \pi^*$ assignment gives three contributions to the B-term.

The high-intensity band at 4.15 μm^{-1} is assigned analogously to that in PtCl₃(C₂H₄)⁻ at 5.21 μm^{-1} , i.e. $\pi \rightarrow x^2-y^2$. The alternative assignment as a singlet-singlet d→ π^* transition is not likely in this case (*vide infra*).

For the d-d transitions in PdCl₃(C₂H₄)⁻ a smaller splitting is observed than for the d→ π^* transitions. This is probably due to differences in the electronic repulsion in both cases. The same effect seems to explain the corresponding differences in d-d vs. d-p transitions in PtX₄²⁻ (X = Cl, Br, I).¹⁴

The extremely strong bands in the 'far'-UV: the presence of singlet-triplet transitions. It has been suggested earlier that the band at 4.15 μm^{-1} [PdCl₃(C₂H₄)⁻] with a very high ϵ_{max} (ca. $3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) should be ascribed to the transition $\pi \rightarrow x^2-y^2$. The arguments for that are based on a comparison with the UV absorption spectrum of PdCl₄²⁻, cf. Refs. 10, 14, 19 and 20. This spectrum consists of two allowed transitions, one very strong ($\epsilon_{\text{max}} \approx 3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) at 4.5 μm^{-1} and one rather strong ($\epsilon_{\text{max}} \approx 1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) at 3.6

μm^{-1} . They have been unambiguously assigned both from solution spectral measurements,^{10,14} including MCD,¹⁹ and from single-crystal reflection measurements.²⁰ Both are ligand to metal charge-transfer (LMCT) transitions; the strong one at $4.5 \mu\text{m}^{-1}$ is ascribed to ligand(Cl)($p\sigma$) $\rightarrow x^2-y^2$ and the other one to ligand(Cl)- $p\pi$ (in-plane) $\rightarrow x^2-y^2$. Concerning the ligand orbitals in $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$, the ethene π orbital can, for symmetry reasons, only combine with the Cl($p\sigma$) orbitals, to build up the four σ MOs, but not with the Cl($p\pi$) (in-plane) orbitals. Since the ionization potential of C_2H_4 (10.5 eV)¹⁶ is smaller than that of a Cl atom (13.2 eV),¹⁶ the resulting four σ MOs should consist of three "low-lying", mainly Cl($p\sigma$), orbitals and one "high-lying", mainly ethene- π , orbital. There must thus exist a LMCT "ethene- π " $\rightarrow x^2-y^2$ transition with a lower transition energy than corresponding LMCTs "Cl($p\sigma$)" $\rightarrow x^2-y^2$. A comparison with the spectra¹⁴ of PdCl_4^{2-} and the isostructural $\text{PdCl}_3(\text{H}_2\text{O})^-$ show that "Cl($p\sigma$)" $\rightarrow x^2-y^2$ corresponds to bands with transition energies $>4.5 \mu\text{m}^{-1}$. The lower transition energy ($4.15 \mu\text{m}^{-1}$) in $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ suggests that it is reasonable to assign that band as suggested, i.e. the LMCT "ethene- π " $\rightarrow x^2-y^2$ transition. However, if the UV spectrum of $\text{PdCl}_3(\text{H}_2\text{O})^-$ is also considered, it is reasonable to believe that the band may correspond to two transitions, the "ethene- π " $\rightarrow x^2-y^2$, and one assigned as ligand(Cl)($p\pi$)(in-plane) $\rightarrow x^2-y^2$ (Ref. 14, Fig. 5 and Table 2). The latter transition cannot alone correspond to the $4.15 \mu\text{m}^{-1}$ band, since the molar absorptivity ($\epsilon_{\text{max}} \approx 3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) is four times higher than for the band(s) in $\text{PdCl}_3(\text{H}_2\text{O})^-$ assigned as ligand(Cl)- $p\pi$ (in-plane) $\rightarrow x^2-y^2$ (ca. $4.2 \mu\text{m}^{-1}$). Such a high ϵ_{max} is reasonable for an allowed transition between orbitals which largely extend over the same region of space (the transition moment integral then has a high value²¹), as ethene- π and x^2-y^2 do for symmetry reasons. Formally, that transition may correspond both to a singlet-singlet and a singlet-triplet transition, but only the former will have any appreciable intensity. This follows immediately from a comparison of the corresponding LMCT transition in PdX_4^{2-} (X = Cl, Br and I), i.e. ligand- $p\sigma$ $\rightarrow x^2-y^2$, which has been discussed elsewhere.¹⁰ Owing to the high symmetry (D_{4h}), there is only one allowed ligand- $p\sigma$ $\rightarrow x^2-y^2$ transition, $2e_u$ (ligand- $p\sigma$) $\rightarrow 3b_{1g}(x^2-y^2)$ or, in state symbols, ${}^1A_g \rightarrow {}^1E_u$. The same orbital transition also corresponds to a formally spin-forbidden singlet-triplet transition, ${}^1A_g \rightarrow {}^3E_u$, and this one is clearly seen in the spectra¹⁴ of the tetrabromo and, especially, tetraiodo¹⁰ complexes but not in the tetrachloro¹⁴ complex. The reason for its gradual appearance in the series X = Cl, Br and I in PdX_4^{2-} has been discussed elsewhere:¹⁰ the spin selection rule ($\Delta S = 0$) is less valid the higher the atomic number (of the halide ligand). Since the atoms in ethene all have atomic numbers lower than that of Cl, this argument means that only the singlet-singlet ethene- π $\rightarrow x^2-y^2$ transition can have any significant intensity in the spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ [and of $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$].

By the same argument the singlet-singlet $d \rightarrow \pi^*$ and $d-d$ transitions in the spectrum of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ should be

accompanied by considerably weaker singlet-triplet $d \rightarrow \pi^*$ and $d-d$ transitions than in $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$. Hypothetically, it can be assumed that the ratio between the intensities (ϵ_{max}) of the singlet-triplet and singlet-singlet $d \rightarrow \pi^*$ transitions are of the same order of magnitude as for the $d-d$ transitions. According to Table 1 that ratio is 10:265 in the case of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ and 10:227¹⁴ for $\text{PdCl}_3(\text{H}_2\text{O})^-$, which means that the value of ϵ_{max} for singlet-triplet $d \rightarrow \pi^*$ should be $<1:20$ of the strongest band (Table 1, $3.81 \mu\text{m}^{-1}$) or $\epsilon_{\text{max}} < 250 \text{ cm}^{-1} \text{ M}^{-1}$, i.e. of the same order of magnitude as the ϵ_{max} of the singlet-singlet $d-d$ transitions. Assuming the same splitting in both cases, i.e. $(2.31-1.95) \mu\text{m}^{-1}$ or about $0.4 \mu\text{m}^{-1}$, cf. Table 1, it is, however, unlikely that the strongest singlet-triplet $d \rightarrow \pi^*$ transition should correspond to a band in the same spectral region as the $d-d$ bands, rather should it be hidden under the $d \rightarrow \pi^*$ bands at 3.28 or $2.81 \mu\text{m}^{-1}$. A hypothetical alternative for $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ is to assign the bands between 2.5 and $4.0 \mu\text{m}^{-1}$ as singlet-triplet $d \rightarrow \pi^*$ transitions. This can be excluded because the corresponding singlet-singlet transitions would correspond to incredibly large absorptivities ($\epsilon_{\text{max}} \geq 1 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$).

Concerning $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$, a similar reasoning must rely on the $d-d$ spectrum of $\text{PtCl}_3(\text{H}_2\text{O})^-$ only, since the $d-d$ assignment for the band around $3 \mu\text{m}^{-1}$ in $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ must be considered uncertain. This results in a ratio between the intensities (ϵ_{max}) of the singlet-triplet and singlet-singlet $d-d$ transitions of about 1:6 ($\approx 19:107$),¹⁴ which suggests that the value of ϵ_{max} for singlet-triplet $d \rightarrow \pi^*$ bands hypothetically could be $\leq 500 \text{ cm}^{-1} \text{ M}^{-1}$. The splitting is ca. $1 \mu\text{m}^{-1}$, which means that such bands hypothetically can give rather large contributions to the absorption between 3.5 and $3.0 \mu\text{m}^{-1}$. Another reasonable alternative for $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ is to assign the bands between 4.16 and $3.44 \mu\text{m}^{-1}$ in accordance with the suggestion by Chang and Zink,¹⁵ i.e. as singlet-triplet $d \rightarrow \pi^*$ transitions. That these bands might have a different origin compared to those of $\text{PdCl}_3(\text{C}_2\text{H}_4)^-$ between 3.81 and $2.81 \mu\text{m}^{-1}$ is indicated by the differences in the MCD spectra (cf. Figs. 3 and 4). The parent singlet-singlet transitions in $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ should then, according to the preceding discussion, correspond to about six times stronger bands (i.e. $\epsilon_{\text{max}} \approx 3 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) in the far-UV region. One possible candidate is obviously the band at $5.21 \mu\text{m}^{-1}$.

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