ZEISE'S ANION AS A SYSTEM
OF STRONGLY ANHARMONIC COUPLED OSCILLATORS*

R.ŘEŘICHA

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Science, 165 02 Prague 6 - Suchdol

A very strong IR absorption near $1020 \ cm^{-1}$ of solid Zeise's salt, $K[(C_2H_4)PtCl_3].H_2O$, is usually splitted into a doublet. This splitting is not reproducible with different samples and depends on a "history" of the sample studied (anhydrous or the monohydrate) and the technique of measurement (suspension in Nujol, KBr or KCl pressed discs, *etc.*). The doublet is assigned to the third overtone of the CC torsion (CH_2 twisting) and to the in-phase CH_2 wagging fundamental frequency. A near-coincidence of the $4\nu_4'$ and ν_7' levels of the same symmetry leads to a Fermi resonance, which explains the strong intensity of the $4\nu_4'$ transition and accounts for the non-reproducibility mentioned. The coordinated ethene represents a non-rigid subsystem due to its chemical pseudoexcitation. A model of the reaction coordinate for formation of Zeise's anion by an intermolecular vibronic interaction is outlined.

Recently[1], the vibrational spectra of anhydrous Zeise's salt (further ZS) have been reinterpreted. Of the vibrational frequencies of ethene, the most prominent change after coordination was deduced for the CC bond torsional vibration (also called the CH_2 twisting). Its frequency falls from the original value of 1023 down to $185 \ cm^{-1}$, the former being the calculated[2] anharmonic frequency of the spectrally inactive ν_4 vibration of free ethene molecule in the electronic ground state. The final value, $185 \pm 5 \ cm^{-1}$, is the experimental fundamental frequency ($1' \leftarrow 0'$) of the CC torsion[1] of coordinated C_2H_4 observed[3] in the inelastic neutron scattering (INS) spectrum of crystalline monohydrate of ZS. Our explanation[1] of this marked lowering is based upon the expectation that a σ-forward-donation of electrons from ethene to Pt reduces the CC bond order (which is manifested by a lowering in the CC stretching frequency from 1623 to 1241 cm^{-1} after coordination) and thus the CC torsional force constant and frequency are also reduced. Furthermore, the rigidity of planar configuration of nuclei in coordinated C_2H_4 is released, the out-of-plane internal vibrations of ethene ligand become large amplitude oscillations, and thus their strong anharmonicity is expected. As a consequence deduced from this model a strong IR band of solid anhydrous ZS and a strong depolarized Raman line of aqueous solutions of ZS, both near $500 \ cm^{-1}$, were assigned to the first overtone ($2' \leftarrow 0'$, $2\nu_4'$) of the CC torsion (and not to the "second Pt—C stretching vibration" in the PtC_2 ring)[1]. The value of about 185 and $500 \ cm^{-1}$ for these vibrational transitions account for a strong positive anharmonicity of the CC torsion in the coordinated species[1].

With free C_2H_4 in symmetry allowed electronic transitions, the non-totally symmetric CC torsion (a_u) is excited with a positive anharmonicity by even number of quanta[1]. Moreover,

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a promotion of one electron from the π orbital (HOMO) releases the rigidity of planar configuration of nuclei and the vibration ν'_4 becomes a torsional oscillation with a large amplitude. The electronically excited ethene is then a non-rigid molecule. The observed[4,5] overtones of ν'_4 in the singlet $3s$ Rydberg state are nearly 500 cm^{-1} $(2\nu'_4)$ and more than 1 000 cm^{-1} $(4\nu'_4)$. As expected, the intensity of $4' \leftarrow 0''$ transition in the free molecule is about eight times weaker[5] than that of $2' \leftarrow 0''$. The assignment of $4\nu'_4$ (1 084 cm^{-1}) was corroborated with the full series of deuterated ethenes[6].

Then, it was deduced[1] that the local electronic state of the coordinated ethene is a local excited state (or a chemically pseudoexcited state[7]) comparable, as its vibrational frequencies and geometry, to some electronic excited (Rydberg)[1,8] state of the free ethene molecule. Such an assignment is somewhat different from the opinion of Chatt[9]: "Now the IR spectra, much better resolved, showed definitely that the ethylene in the platinous complex was essentially unchanged."

Applying the above mentioned facts to a chemically pseudoexcited state of the coordinated C_2H_4, the appearance of ν'_4 overtones higher than 500 cm^{-1} can be expected in the IR spectrum of ZS, especially $4\nu'_4$ near 1 000 cm^{-1}. Eventually, the possibility of tunnelling splitting of these vibrational levels in non-rigid ethene ligand can be taken into consideration[10].

The aim of this work is to summarize published experimental data about the vibrational spectra of ZS and to supplement them by absorption measurements in the near IR region, with respect to the (originally) out-of-plane vibrations of the ethene coordinated in Zeise's anion.

EXPERIMENTAL

Preparation of anhydrous ZS was described earlier[11]. The IR absorption spectra of anhydrous ZS in Nujol suspension and in KBr or KCl pressed discs were recorded on the following double-beam instruments: Beckman IR-7 (grating, up to 4000 cm^{-1}), Zeiss (Jena) UR-20 (LiF prism, up to 5000 cm^{-1}), and Beckman DK-2A (SiO$_2$ prism, around 10000 cm^{-1}).

RESULTS AND DISCUSSION

As it was mentioned in the Introduction, the appearance of an absorption band around 1 000 cm^{-1} can be expected for the third CC torsion overtone $(4\nu'_4)$ and, moreover, the band could be splitted. Indeed, a doublet was observed by many authors, however, with a much higher intensity than expected for an overtone. In fact, this doublet represents the strongest IR absorption of solid ZS in the 4000$-$400 cm^{-1} region. The published experimental data are summarized in Table I, the problem of the strong intensity and assignment of the doublet will be dealt with later.

The mean positions of the doublet near 1 000 cm^{-1} are in the range of 1 028·5 to 1 016 cm^{-1}, regardless whether the studied sample of ZS was anhydrous (1 028·5 to 1 017·5 cm^{-1}) or the monohydrate (1 026$-$1 016 cm^{-1}). The spread of the data is noticeable and, hence, incorrect calibrations of the wavenumber scales of the instruments used can be considered. However, this possibility is easily eliminated by the inspection of new and earlier data (grating instruments 1 028·5 to 1 016 cm^{-1}

TABLE I

The Very Strong IR Doublet near $1\,000\ cm^{-1}$ in Solid Zeise's Salt, its Assignment, and Experimental Conditions

Doublet and intensity	Separation cm^{-1}	Mean position cm^{-1}	Zeise's salt[a]	Technique	I[b]	Assignment[c]	Ref.
1 022 s 1 010 s	12	1 016	H_2O	Nujol	P	none	26
1 023 s 1 011 s	12	1 017	H_2O	Nujol	P	none	27
1 030 vs 1 022 vs	8	1 026	H_2O?	KBr	P?	none	28
1 022 s 1 010 s	12	1 016	H_2O	Nujol	P	ν_7 and ν_8	11, 29
1 032 s 1 024 s	8	1 028	anh.	Nujol	P	ν_7 and ν_8	14
1 025 s 1 015 s	10	1 020	H_2O	Nujol	P	$(\nu_7$ and $\nu_4)^d$	30
1 024 1 009	15	1 016·5	?	?	G?	ν_7 and ν_8	31, 32
1 032 1 024	8	1 028	anh.	?	?	ν_7 and ν_8	33, 34
1 023 vs	0	1 023	H_2O	KBr	G	ν_7 and ν_8	12
1 023 vs 1 012 vs	11	1 017·5	anh.	Nujol, KCl	G	ν_7 and ν_8	35
1 022 vs 1 010 vs	12	1 016	H_2O	Nujol	G	CH_2 wag.	15
1 025 vs 1 010 sh	15	1 017·5	H_2O	Nujol	G	CH_2 wag.	36
1 032 vs 1 025 vs	7	1 028·5	anh.	Nujol	G	CH_2 wag.	36
1 032 vs 1 025 vs	7	1 028·5	anh.	KCl, Nujol	G	$(\nu_7'$ and $4\nu_4')^e$	this work
1 016 vs 1 009 vs	17	1 017·5	anh.	KBr	G	ν_7 and ν_8	35(PtBr$_3$)
1 020 sh 10 16 vs	4	1 018	anh.	Nujol	G	CH_2 wag.	36(PtBr$_3$)

[a] H_2O means monohydrate, anh. means anhydrous; [b] I means instrument: P — prism, G — grating; [c] notation of vibrations according to Herzberg[10], i.e., z-axis is perpendicular to the C_2H_4 molecular plane; [d] from ref.[37]; [e] the single primed quantities are related to the chemically pseudo-excited state of ethene.

vs prism instruments $1028 - 1016$ cm^{-1}). The only difference in the data which can be found relates to the technique of measurement of the solid monohydrate of ZS: $1026 - 1023$ cm^{-1} (2 cases of KBr tablets) and $1020 - 1016$ cm^{-1} (6 cases of Nujol suspensions).

As to the observed separations of doublet maxima $(0 - 15$ cm$^{-1})$ no trend was found but, strikingly, the separations do not depend on the type of instruments used: prism instruments $8 - 12$ cm^{-1}, most of the grating instruments $7 - 15$ cm^{-1}, with the only exception of the data reported by Grogan and Nakamoto[12] who observed one unsplitted IR band at 1023 cm^{-1} (Beckman IR-12 grating instrument). Moreover, the relative intensities in the doublet maxima are also variable (Table II). Summarizing, the observed effects (variable location of the doublet, separation of its maxima, and their relative intensities) seem to originate from treatment of the samples of ZS, *i.e.*, the cause lies in the "history" of the samples[13]. At this moment it can be noted that the pattern of the absorption near 1000 cm^{-1} is not too typical for a fundamental vibrational transition alone.

The first assignment of the strong doublet near 1000 cm^{-1} is due to Powell and Sheppard[14] who ascribed it to the fundamental frequencies of the wagging vibrations of both $=CH_2$ groups, *i.e.*, the in-phase (v_7 or v_{12} after Herzberg or Mulliken, resp.) and the out-of-phase wagging motions (v_8 or v_7 after Herzberg or Mulliken, resp.). They assumed that the Pt--C_2H_4 coordination bond represents a relatively weak interaction, and with the free ethene molecule in its electronic ground state the cor-

TABLE II
Relative Intensities in the Maxima of the Doublet near 1000 cm^{-1}

Zeise's salt	Technique	Intensity of of HW band[a]	Ref.
Anh.	Nujol	equal	14
H_2O	Nujol	weaker	29
Anh.	KBr	weaker	35
H_2O	Nujol	stronger	35
H_2O[b]	KCl	weaker	
Anh.[c]	KCl	weaker	} this work[e]
Anh.[d]	KCl	stronger	

[a] HW denotes higher wavenumber. [b] Needle crystals. [c] Needle crystals dried in an evacuated desiccator over KOH. [d] Powder remaining after fast removal of aqueous HCl by evacuation. [e] Our preliminary measurements of the IR spectrum at different temperatures showed that the relative intensities can be reversed (anhydrous ZS in KCl disc below room temperature down to $-160°C$). The change with temperature is reversible.

responding fundamentals are also close together (at 949 cm^{-1}, infrared active, and 943 cm^{-1}, Raman active). Most of the authors adhered to this assignment, including Grogan and Nakamoto[12], who interpreted the single band at 1023 cm^{-1} as an accidental coincidence of the v_7 and v_8 fundamentals in the coordinated species. However, the measurement of the laser Raman spectrum of an aqueous solution of ZS led to a change in the assignment[15], since a single line at 1021 cm^{-1} was observed instead of a doublet. A similar situation has been encountered in the IR spectrum of a solution of ZS in acetone[15]. Hence, it was concluded[15] that the IR doublet near 1000 cm^{-1} for solid ZS is to be due to crystal state effects on the out-of--phase wagging vibrational level (Herzberg's v_8), the v_7 level being at a lower value (975 cm^{-1}). Despite of this, in another paper[16] dealing again with the laser Raman spectrum of an aqueous solution of ZS, a doublet near 1000 cm^{-1} was recorded (cf. Fig. 1 in ref.[16]). Therefore, a crystal state effect need not be considered as the only and direct reason for the splitting of the band near 1000 cm^{-1}. Concluding, it is noteworthy that the geometrical out-of-plane distorsion of the coordinated ethene had a form of the in-phase CH$_2$ wagging mode v_7.

Summarizing the published data, the possible explanation of the strong IR doublet of solid ZS near 1000 cm^{-1} can be proposed. A near-coincidence of the v_7' and $4v_4'$ quanta leads to a Fermi resonance between the corresponding in-phase CH$_2$ wagging and the CH$_2$ twisting (CC torsion) vibrational levels of the same symmetry (a_1 for
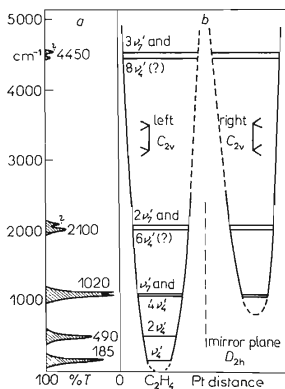

Fig. 1

A Schematic Representation of the v_7' and v_4' Vibrational Levels in the Coordinated C$_2$H$_4$

a The relevant parts of the IR absorption spectrum of solid Zeise's salt: the band near 185 cm^{-1} is for the monohydrate (inelastic neutron scattering[3] and IR absorption[12]); the band at about 490 cm^{-1} is for the anhydrous salt[14,15,35,36,41]; for the doublet near 1020 cm^{-1} cf. Table I; the dubious doublets near 2100 and 4450 cm^{-1} are for the anhydrous salt (Nujol, KCl, KBr; the intensities are exaggerated; cf. text). b A hypothetical double minimum potential curve for the in-phase CH$_2$ wagging vibration v_7' of the non-rigid C$_2$H$_4$ ligand. The relative position of both minima and the shape of potential barrier between them are dependent on the Pt—C$_2$H$_4$ distance, i.e., on the amplitude of the Pt—C$_2$H$_4$ stretching vibration. For simplicity, the v_4' levels (CC torsion or CH$_2$ twisting) are included to indicate the assumed coupling between v_4' and v_7'.

C_{2v}). Hence, instead of a strong band and a weak one, which can be otherwise reasonably expected, the strong doublet with roughly equal intense branches is observed. The third overtone $4v_4'$ borrows its intensity from the v_7' fundamental, so becoming even more intense than the first overtone $2v_4'$ near 500 cm^{-1}. At this moment the effect of environment on Zeise's anion can be taken again into consideration, offering a model which can account for the variable shape of the band near 1000 cm^{-1}. Changes of the defined crystal structure of the monohydrate after its dehydration and/or its suspending in Nujol, pressing in alkali halide discs under different pressures or its dissolution *etc.* influence the v_7' and $4v_4'$ levels. Even small changes in their relative positions strongly affect the interaction, resulting in the above mentioned experimental facts. Such a doublet near 1000 cm^{-1} is also observed in other ethene complexes, *e.g.*, in neutral Zeise's dimer and in its palladium analogue[13–15]. In the case of C_2D_4 coordinated in ZS, however, the $4v_4'$ (estimated 1000–900 cm^{-1}) and v_7' levels (around 700 cm^{-1}) are well separated.

If this assignment of the strong IR doublet near 1000 cm^{-1} is plausible the appearance of other doublets can be expected in the IR spectrum of ZS around 2100, 4500 cm^{-1} and so on, these being, however, of much lower intensity. In the 2100 to 2000 cm^{-1} region one very weak IR band has been observed by several authors, in earlier papers another one has been found around 2300 cm^{-1}. The latter can be reasonably ascribed to an incomplete compensation of atmospheric CO_2 in the instruments. The only work which quotes two weak absorptions (2098 and 2048 cm^{-1}) is that of Grogan and Nakamoto[12]. We also observed in some samples of anhydrous ZS (KCl and KBr discs, Nujol) two bands at 2125 and 2060 cm^{-1} to which another pair near 4600 and 4480 cm^{-1} corresponds. Around 10000 cm^{-1} our tablets were opaque, concentrated aqueous solutions of ZS showed only absorptions due to H_2O in this region. With another samples of ZS we observed only one asymmetric band near 2100 and 4400 cm^{-1} or the band with a shoulder at the same wavenumbers. However, the reliability of very weak absorptions is rather low with respect to possible impurities (*e.g.*, Pt—C≡O around 2000 cm^{-1}). Thus, assuming that the asymmetric band near 2100 cm^{-1} is not due to impurities, these absorptions can be regarded as another member of Fermi diads, *i.e.*, $2v_7'$ and $6v_4'$, an analogous interpretation could hold for the two absorptions near 4450 cm^{-1} (Fig. 1). The non-reproducibility of the spectral pattern around 2100 and 4500 cm^{-1} is in line with our proposed interpretation of the doublet near 1000 cm^{-1} but, simultaneously, the agreement could be only apparent. This ambiguity should be clarified by additional studies of several independently prepared samples of ZS.

Little attention was paid to the fundamental frequency of the out-of-phase wagging vibration, v_8', of the coordinated ethene. The reason can be found in the IR spectra of 1-alkene analogues of ZS (Table III, *cf.*[11]). These spectra show also a doublet near 1000 cm^{-1}, although both wagging fundamental frequencies are well separated in free 1-alkenes (about 900 and 600 cm^{-1})[17] in comparison with free ethene (949

Table III

The IR Doublet near $1\,000\ cm^{-1}$ in Solid 1-Alkene Analogues of Zeise's Salt

Coordinated 1-alkene	Doublet and intensity	Separation cm^{-1}	Sample	Technique	I	Ref.
Propene	1 010 m 990 m	20	H_2O	Nujol	P	26, 38
Propene	1 014 s 994 s	20	H_2O	Nujol	P	30
1-Decene-d_0	1 009 m 993 m	16	anh.	KCl	G	11
1-Decene-2-d_1	1 010 m 994 m	16	anh.	KCl	G	11
1-Decene- -trans-1-d_1	947 m 933 m	14	anh.	KCl	G	11

Table IV

The Published Assignments of the Vibrational Frequency of ZS at about $180\ cm^{-1}$

Band, intensity	Zeise's salt[a]	Technique	Assignment[b]	Ref.
181 m	?	IR, Nujol	in-plane def. $PtCl_3$	40
183 s	H_2O	IR, polyethylene	in-plane def. Cl—Pt—Cl	12
181 m	H_2O, anh.	IR, Nujol	in-plane def. Cl—Pt—Cl	35
180 (50/100)[c]	anh.	Ra, crystal. powder	in-plane def. Cl—Pt—Cl	36
181 m	H_2O	IR, Nujol	$\left.\begin{array}{l}\text{PtCl}_2 \text{ bend. or}\\ \text{PtCl}_1 \text{ bend. or}\\ \text{PtCl}_2 \text{ wag. or}\\ \text{PtC}_2 \text{ twisting}\end{array}\right\}$	
177 (2/10)[c]	H_2O	Ra, crystal		15[d]
171 (dep.)[c]	aq. soln.	Ra, aq. soln.		
185 ± 5 (s)[e]	H_2O	INS, crystal	$\left.\begin{array}{l}\text{rotation of } C_2H_4 \text{ with}\\ \text{respect to } PtCl_3 \text{ plane}\end{array}\right.$	3
185 ± 5 (s)	H_2O	INS, crystal	CC torsion (ν_4') fundamental	1 and this work

[a] Monohydrate or anhydrous solid; [b] cf. also[39]; [c] Raman line; [d] formation of a three-membered heterocyclic PtC_2 ring has been assumed[15]; [e] inelastic neutron scattering[3], the assignment based on assumed PtC_2 ring formation[15].

and 943 cm^{-1}). So, the doublet near 1000 cm^{-1} can be hardly interpreted as being due to "close" fundamentals, which case was possible with the coordinated C_2H_4. In contrary, this strong doublet can similarly be assigned to a Fermi doublet involving the in-phase wagging fundamental and the third CC torsion (CH$_2$ twisting) overtone frequencies. The location of the doublet is nearly the same for 1-decene-d_0 and 1-decene-2-d_1 complexes, so indicating that it is characteristic for the $=CH_2$ terminal group. In the case of 1-decene-*trans*-1-d_1 complex the doublet is shifted to lower wavenumbers, in other cases of the partially or fully deuterated vinyl group it is missing in the IR spectra. Therefore, we leave the value of the ν'_8 fundamental for the coordinated ethene indeterminate.

Let us turn our attention to the low wavenumber region of the IR spectrum of ZS. There is a question whether the fundamental transition of the CC torsion, found in the INS spectrum[1,3], is infrared-active or -inactive (a_u, a_2, a'' for D_{2h}, C_{2v}, C_s, resp.). In other words, whether an absorption band near 185 cm^{-1} is present in the IR spectrum, and if so, what is its assignment. The relevant data are summarized in Table IV. It is clear that a medium to strong IR absorption has been observed by many authors between 183 − 181 cm^{-1}. In all cases this band is assigned to a fundamental frequency of the PtCl$_3$ moiety of Zeise's anion, without considering any connection with the vibrations of the C_2H_4 ligand. However, all the mentioned interpretations have followed normal coordinate analyses of the separated PtCl$_3$ fragment. If our assignment of the 185 ± 5 cm^{-1} frequency (from the INS spectrum) to the CC torsion fundamental (ν'_4, $1' \leftarrow 0'$) is essentially correct, then a strong mixing of PtCl$_3$ and C_2H_4 vibrational motions can be anticipated in the corresponding IR
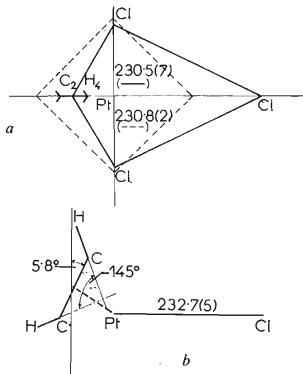

Fig. 2

The Crystallographic Geometries of the Anions PtCl$_4^{2-}$ (square) and [(C_2H_4)PtCl$_3$]$^-$ (deltoid)

Exaggerated by a large factor; the numerical values (in picometers, pm) are from refs[18,19,42]. *a* Top view. *b* Front view. The out-of-plane deformation of C_2H_4 ligand has the form of the in-phase CH$_2$ wagging vibration ν_7.

absorption. Instead of the preference of either fragment in the assignment, it seems more reasonable to consider vibrational coupling of both parts of Zeise's anion. Under such assumption, the 185 cm^{-1} mode can be regarded as the common "tuning" frequency for the coupling of both non-separable fragments.

Let us begin with a comparison of geometries of the starting $PtCl_4^{2-}$ and resulting Zeise's anion, $[(C_2H_4)PtCl_3]^{(-)}$, cf. Fig. 2. The original square planar configuration of Cl atoms around central Pt (dashed line[18]) changes after replacement of one chlorine by ethene to a deltoid (neglecting for this moment that the midpoint of the CC bond is 20 pm above the $PtCl_3$ plane[19]). Whilst the bond lengths of trans-Cl---Pt—Cl grouping remain practically unchanged, the Pt—Cl bond opposite to ethene is markedly lengthened[19]. The deltoidal distorsion of the square has a form of one of the Pt—Cl stretching vibrations of the originally degenerated pair v_{6b}. Moreover, it indicates the feasibility of dissociation of one Pt—Cl bond in the course of the substitution reaction[20]

$$PtCl_4^{2-} + C_2H_4 \xrightarrow{\text{fast}} [(C_2H_4)PtCl_4]^{2-} \xrightarrow{\text{slow}} Cl^{(-)} + [(C_2H_4)PtCl_3]^{(-)}$$
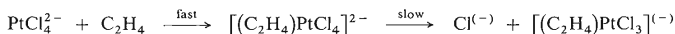
So, one of the vibrations of the v_{6ab} pair could participate in a model of the reaction coordinate for formation of Zeise's anion.

From the survey of the normal vibrations of $PtCl_4^{2-}$ in Table V is clear that two of them can be the Jahn–Teller active modes[21]. However, it has been pointed out[22]

TABLE V
Normal Vibrations of Square Planar $PtCl_4^{2-}$ $(D_{4h})^a$

No	S^b	Fundamental cm^{-1}, act.		Form^c	Note
v_1	a_{1g}	333	(Ra)	(i-p) stretch.	
v_2	a_{2u}	168	(IR)	(o-o-p) def.	
v_3	b_{1g}	306	(Ra)	(i-p) stretch.	Jahn–Teller active[21]
v_4	b_{1u}	128	(ia)	(o-o-p) def.	inactive, calculated[43]
v_5	b_{2g}	196	(Ra)	(i-p) def.	Jahn–Teller active[21]
v_{6a} v_{6b}	e_u	321	(IR)	(i-p) stretch.	geometry of Zeise's anion
v_{7a} v_{7b}	e_u	191	(IR)	(i-p) def.	"tuning" frequency?

^{a} From[43,44]; ^{b} S means symmetry, the axes x and y are oriented along the trans Cl—Pt—Cl bonds; ^{c} i-p means in-plane, o-o-p out-of-plane.

that "the (geometrical) instability is only slight if the (orbital) degeneracy is due solely to electrons having no great influence on the binding of the molecule". Just it is the case of doubly degenerated $5e_g$ molecular orbitals (HOMO-1) of $PtCl_4^{2-}$, which were interpreted[23] as "d-like atomic" orbitals ($5d_{xz}$ and $5d_{yz}$) of the central Pt^{2+} ion. The character of these occupied group orbitals is only slightly antibonding so that no static Jahn–Teller distorsion of the square-planar $PtCl_4^{2-}$ is observed. In an interaction of planar $PtCl_4^{2-}$ with planar ethene, however, the picture of bonding in $PtCl_4^{2-}$ is completely changed. Even in a long-range interaction of both species, when their local point symmetries D_{4h} and D_{2h} are still applicable, the mutual degeneracy of $5e_g$ MO's of $PtCl_4^{2-}$ can be gradually removed by a dynamic instability of the square. The resulting distorsion along one or the other vibrational coordinate (b_{1g} or b_{2g}, cf. Table V) will depend upon the initial orientation of ethene molecule with respect to the square (in Fig. 3 the interacting species are in parallel planes
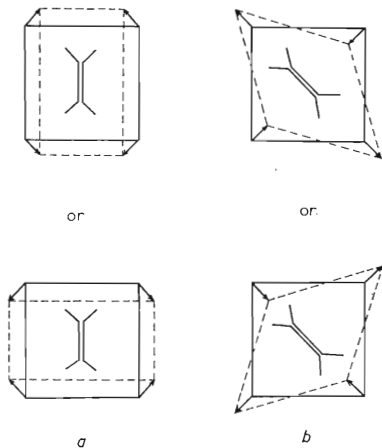

or

or

a

b

FIG. 3

The Top View of the Jahn–Teller Distorsions of the Square-planar $PtCl_4^{2-}$ after an Interaction with C_2H_4 in a Parallel Plane

a Rectangular (due to the in-plane $PtCl_4^{2-}$ deformation vibration, originally b_{2g}). b Orthorhombic (due to the stretching vibration, originally b_{1g}). The axes x and y are oriented along the $trans$-Cl—Pt—Cl bonds. If x and y bisect the cis-Cl—Pt—Cl angles, the notation is reversed: b_{1g} is rectangular and b_{2g} is orthorhombic.

with collinear z-axes). An orthorhombic distorsion reveals intuitively the form more convenient for formation of Zeise's anion. In any case, both possibilities in Fig. 3a,b represent a weak vibronic interaction of the type $E \otimes \beta$ ($cf.^{24,25}$) which will dynamically remove the orbital degeneracy of $PtCl_4^{2-}$ and cause a descent in overall symmetry of the interaction complex to (at least) C_{2v}. When the molecular planes of interacting $PtCl_4^{2-}$ and C_2H_4 are not parallel, the regular orthorhombic distorsion of the square becomes a deltoidal one (due to v_{6a} or v_{6b}, $cf.$ Fig. 3b) and this distorsion can lead to dissociation of one Pt—Cl bond and to substitution by C_2H_4. Consequently, some of the non-genuine vibrations of ethene ($i.e.$, translations and rotations) in the force field of $PtCl_4^{2-}$ become the genuine vibrations of the interaction complex before Zeise's anion is formed. These modes will also be involved in this model of reaction coordinate along with the internal vibrations of C_2H_4 (in its local point symmetry C_{2v} and in the original Herzberg's notation, these are: v'_1, v'_2, v'_3, v'_7, and nv'_4 for n even).

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* Translated by the author.

Note added in proof:

Erratum: In the previous paper[1], *the following corrections should be made: 1. Line 19 from top of p. 2588 should be read: "Apparently, at least a four-center MO is formed...", 2. The first sentence of the last paragraph on p. 2589 should be read: "Whilst the first radical cation or the π* states...".*