

RE-INTERPRETATION OF THE VIBRATIONAL SPECTRA OF ZEISE'S SALT. THE NATURE OF THE Pt-ETHENE BOND*

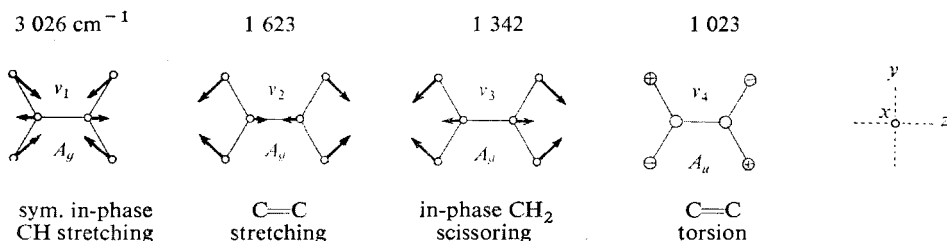
R.ŘEŘIČHA

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

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It is shown that the local electronic state of ethene coordinated in Zeise's salt (further ZS), $K_2[PtCl_3(C_2H_4)] \cdot H_2O$, is comparable to some electronic excited states of the free molecule. The forward-donation of a π -electron from ethene to Pt reduces the CC bond order to about 1.5 and the CC stretching frequency to 1241 cm^{-1} . The "depolarized" line of ZS at 492 cm^{-1} is interpreted as the first overtone ($2\nu_4$) of the CC torsion, the fundamental of which drops to 185 cm^{-1} (by inelastic neutron scattering). The polarized line of ZS at 404 cm^{-1} represents the stretching fundamental of one and only Pt-ethene bond through which both fragments are vibrationally (and perhaps vibronically) coupled together. The π^* orbital of ethene is excluded as the terminating level for the electron back-donated from Pt. Instead, the prevailing population of Rydberg MO's of ethene is considered. The local electronic state of coordinated ethene can then be regarded as the core of a doubly excited radical anion of the free species or as a near-radical-cation.

A molecule of free ethene in the electronic ground state and equilibrium configuration of nuclei¹ is planar, has the center of symmetry, and belongs to the point group D_{2h} . Of the twelve normal vibrations, three are of A_g symmetry (Raman active), one is the inactive A_u species (Scheme 1;



SCHEME 1

the fundamental frequencies are for C_2H_4). The A_g modes are coupled together and the GHFF analysis revealed² that a relatively strong coupling ($f_{CC}^{def} = -0.289\text{ mdyn/\AA}$) exists between the C=C stretching ($f_{CC} = 9.395\text{ mdyn/\AA}$) and in-phase CH_2 scissoring vibrations ($f_{def} = 0.399\text{ mdyn/\AA}$).

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Information about free ethene in electronic excited states offers its UV spectrum. In the ground state, the HOMO is $1b_{3u}$ which corresponds to the π -bond between the two C atoms. First UV absorptions are due to promotions of one electron from the π -bond to higher levels¹. A removal of this electron from the HOMO weakens the CC bond (3 instead of 4 bonding electrons³, i.e., the bond order decreases from 2 to about 1.5) and means a considerable loosening of the stability of the planar configuration³. It has several consequences: a change in the equilibrium geometry^{1,3-5}, substantial reductions in frequencies ν_2 and ν_4 , the latter being more pronounced from 1023 to about 400 cm^{-1} for the (3s) Rydberg^{1,3-5} or the first ionic state⁶. Finally, changes of the original vibrational couplings and formation of new ones will result^{1,4-6}. With deuterated species, unusual upward shifts of some frequencies, compared to the undeuterated molecule, can occur after the removal of one electron from the π -orbital. This was observed in the UV photoelectron spectra⁶ (UPES) of C_2H_4 and C_2D_4 for ν'_2 in the first ionic ground state: $1290 \rightarrow 1370\text{ cm}^{-1}$, resp. (The doubly primed quantities refer to the ground state, those singly primed or with an asterisk are related to excited states.) Similar upward shifts were observed in the far UV spectra of deuterated 2-methylpropenes⁷:

$$1392(d_0) \rightarrow 1461(1,1-d_2) \quad \text{and} \quad 1389(d_0) \rightarrow 1432\text{ cm}^{-1}(d_8).$$

Recent crystallographic data for ethene coordinated in ZS were obtained by X-ray (XD) (ref.⁸) and neutron diffraction (ND) (ref.⁹). They revealed that the CC bond length is 1.34 to 1.40 (XD) (ref.⁸) and 1.34–1.37 Å (ND) (ref.⁹). From this it follows that sp^2 -hybridization of C atoms is retained rather than changed to sp^3 . The H atoms of coordinated C_2H_4 lie precisely in a plane, both C atoms, however, are out of it toward the Pt atom by 0.18 Å. Thus the hydrogens bent back significantly⁹ and the local symmetry of coordinated ethene is C_{2v} . The angle between the CC bond and PtCl_3 plane is 84.2° with the midpoint of the bond 0.20 Å above the plane⁸. The distances Pt—C(1) and Pt—C(2) are different, 2.13 and 2.14 Å, resp.⁸. Due to these facts, the overall symmetry of the anion descends to C_s (cf.¹⁰).

The laser Raman spectrum of undeuterated ZS in aqueous solutions reveals a very strong polarized band at 1241 cm^{-1} which was assigned¹² to ν_2 of the coordinated C_2H_4 . As to the d_4 species, the corresponding band has been found at 1353 cm^{-1} with a lowered intensity. The ν_2 upward shift $1241 \rightarrow 1353\text{ cm}^{-1}$ due to coordination of C_2D_4 was explained^{12,6} by a loosening of the original vibrational coupling between ν_2 and ν_3 in the molecule. This assignment of ν_2 has been approved several times^{13,14}. On this ground, it was concluded⁶ that there is an analogy between the free radical cation of ethene and ethene coordinated in ZS. Changes in the vibrational coupling between the C=C stretching and CH_2 scissoring vibrations after deuteration and coordination have been repeatedly found¹⁵ in alkenic analogues of anhydrous ZS, including propene- d_0 and $-d_6$ or the full series of the seven stereospecifically deuterated 1-decenes-1,2- d_x ($x = 0-3$).

In the vibrational spectra of ZS- d_0 (IR spectrum of anhydrous powder^{10,12} and laser Raman spectrum of aqueous solution¹²) a couple of bands near 400 (polarized) and 490 cm^{-1} (depolarized) was observed. It has been assumed¹⁰ that the vibrational frequencies of coordinated ethene do not change markedly unless drastic changes occur in its structure and bonding¹⁰. Preferring the first possibility, the authors¹⁰ concluded: "The lowest frequency mode (of free ethene), the CH_2 rocking, absorbs at 810 cm^{-1} and therefore it is safe to assume that all the ethene vibrations (after coordination) will occur above 600 cm^{-1} ". The authors¹⁰ assigned the IR band near 400 cm^{-1} to the stretching vibration of one and only (relatively weak) Pt-ethene bond by analogy with other alkenic Pt complexes¹¹. The other IR band near 490 cm^{-1} has a variable intensity depending on procedure of dehydration of samples so that it has been assigned¹⁰ to a combination

or overtone frequency of a vibration which is sensitive to structural changes of the complex. The authors¹⁰ have not specified this vibration any further.

Of the possibilities, it could be a vibration of PtCl_3 group or of the crystal lattice, or "drastic changes in structure and bonding of ethene"¹⁰. Hiraishi¹² studying aqueous solutions of ZS considered the first possibility and, on the ground of data for Zeise's dimer $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$ and $\text{K}[\text{PtBr}_3(\text{C}_2\text{H}_4)]$, changed the assignment of the 490 cm^{-1} band which is found in spectra of all these compounds: "It is difficult to explain this as a combination because the far IR spectra of these complexes are different from each other... These facts show that the band around 490 cm^{-1} is connected with the Pt-ethene group" and concluded¹²: a three-membered PtC_2 ring is formed, the 404 cm^{-1} polarized line belongs to the symmetrical stretching vibration of the PtC_2 ring, and the depolarized line at 492 cm^{-1} to the antisymmetrical one (assuming the point group of symmetry C_{2v} for Zeise's anion¹²). This model of a tight bond between Pt and ethene, analogous to ethylene oxide¹⁶⁻¹⁹, was accepted by some authors^{20,21}, sometimes with a hesitation^{22,23}.

The aim of this work is to correlate various data for free and coordinated ethenes obtained by different physical methods. The compiled data will serve to a re-consideration of plausibility of the older models by Babushkin-Hiraishi and Chatt-Duncanson²⁴.

RESULTS

A survey of the CC stretching frequencies of free ethene in different electronic states is in Table I. It is clear that the removal of one π -electron from the original C=C bond leads to a significant lowering of ν_2 regardless whether the transition is $T \leftarrow N$, $V \leftarrow N$, $R \leftarrow N$, or $I \leftarrow N$. The coordination to Pt atom in ZS has a very similar effect on ν_2 . Furthermore, such an analogy is much closer for the first radical cation owing to the ν_2 upward shift in d_4 species. The ground state ${}^2B_{3u}$ of the cation represents the convergence limit of preceding (ns), (np), and (nd) series of Rydberg states in free species so that gradual changes in ν_2 frequency and in the vibrational coupling between ν_2 and ν_3 can therefore be expected for increasing values of $n > 3$.

The changed equilibrium geometry of coordinated ethene⁹ (local symmetry C_{2v}) is also in accord with the changes deduced from experiments for different electronic states of the free species^{1,4,5} (D_{2d} or D_2) comparing them to the ground state (D_{2h}). From these facts, a lowering in the CC bond order of coordinated ethene can be anticipated. Accordingly, the semiempirical SCF MO calculation²⁵, including all the valence electrons in Zeise's anion, gave the value of 1.545 for the CC bond order.

In free excited ethene, the lowered CC bond order strongly influences another vibration of the molecule, namely¹ the CC torsion ν_4 , also called the C=C twisting or CH_2 twisting or generally CH_2 out-of-plane deformation A_u . Also the original high barrier to internal rotation around the C=C bond (65 kcal/mol , *cf.*¹, *i.e.*, about 22700 cm^{-1}) is markedly reduced in excited states, *e.g.*, to $290 \pm 20\text{ cm}^{-1}$

in the $3sR$ state⁴. As consequences, the equilibrium geometry of the excited molecule is changed compared to the ground state and ν'_4 becomes the vibration with a large amplitude¹. According to the symmetry selection rules, ν'_4 should be excited by even number of quanta ($A_u \cdot A_u = A_g$) to be active in the symmetry allowed transitions¹. The observed frequencies of C_2H_4 in the $3sR$ state⁴ (468 cm^{-1}) and in the first radical cation⁶ ($405 \pm 30\text{ cm}^{-1}$) are then interpreted as the second harmonics (first overtones, $2\nu'_4$) of the $(CC)^*$ torsion. From this point of view, one of the two IR bands¹²⁻¹⁴ near 400 and 490 cm^{-1} of anhydrous $K[PtCl_3(C_2H_4)]$ could belong to the torsion of the weakened $(CC)_{\text{coord.}}$ bond and not to a second stretching vibration of the assumed PtC_2 ring in the complex. As it was pointed out^{10,11}, the intensity of the IR band near 490 cm^{-1} is sensitive to a procedure of dehydration of samples so that the band could represent a combination frequency or an overtone. We also observed a similar behaviour of an IR band around 520 cm^{-1} in the case of 1-decene-1,2- d_x analogues of anhydrous ZS, namely its intensity changes in Nujol suspensions compared to pressed KCl discs¹⁵. Therefore, we support the original proposals of Grogan and Nakamoto^{10,11} and we retain the assignment of the band near 400 cm^{-1} to the fundamental frequency of one and only Pt-ethene stretching vibration. The other band near 490 cm^{-1} we assign to the second harmonic frequency $2\nu'_4$ (the first overtone $2' \leftarrow 0'$) of the $(CC)_{\text{coord.}}$ torsion. Accordingly, the position of a band near 490 cm^{-1} will not be too sensitive to changes in composition of the anion $[PtX_3(C_2H_4)]$,

TABLE I
The Experimental CC Stretching Frequencies in Different Electronic States of Ethene (cm^{-1})

Electronic state	C_2H_4	C_2D_4	
$^1A_{1g}$ (N , ground, π) ^a	1 623	1 515	
$^1B_{1u}$ (V , singlet π^*) ^b	852 ^c	550—797 ^d	
$^3B_{1u}$ (T , triplet π^*) ^e	995	— ^f	
$^1B_{3u}$ ($3sR$, first Rydberg) ^{b,g} , ν'_2	= 0	1 370	1 295
	= 1	1 349	1 284
	= 2	1 324	1 267
	= 3	1 310	1 240
	= ? ^h	1 280 ^h	— ^f
$^2B_{3u}$ (I , first radical cation) ⁱ	1 290	1 370	
? (coordination to Pt) ^j	1 241	1 353	

^a Raman, gas⁴⁷. ^b Vacuum UV, gas. ^c Ref.⁴⁸. ^d Uncertain¹. ^e Near UV, liquid or gas enhanced by O_2 , refs^{49,50}. ^f Not measured. ^g Rydberg MO in the semi-UAO approximation¹; ν'_2 -vibrational quantum numbers of ν'_2 in the excited state⁴⁸. ^h Ref.^{49,51}, $\pm 60\text{ cm}^{-1}$. ⁱ UPES of gas⁶, $\pm 30\text{ cm}^{-1}$. ^j Laser-Raman spectrum of aqueous solution of Zeise's salt¹².

i.e., only slight variations should occur for the bromo-analogue and even for Zeise's dimer. This is consistent with the experimental findings¹² (near 480 cm^{-1}). Thus, the band around 490 cm^{-1} seems to be really connected with the Pt-ethene group as proposed by Hiraishi¹², however, drastic changes in ethene structure and bonding should be considered as it was stipulated earlier by Nakamoto^{10,11}.

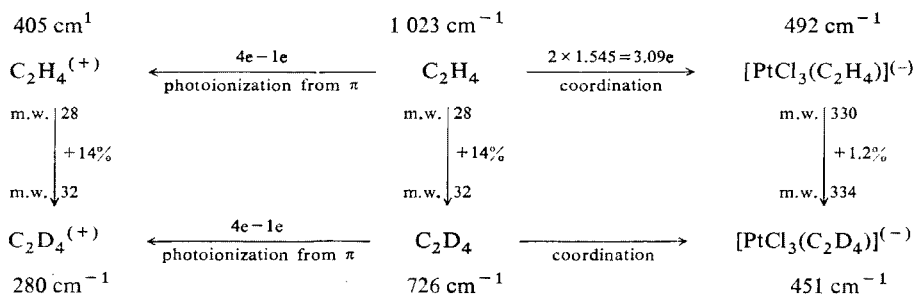
Now, it is necessary to give precision to the fundamental torsional frequency of the (CC)* bond with an order reduced to about 1.5. In free excited ethene, namely in the (*ns*) Rydberg states ($n \geq 3$), the (CC)* torsion fundamental was estimated to be roughly 200 cm^{-1} . Neglecting the anharmonicity of ν_4 , Herzberg³ gives halves of the observed $2\nu_4$ frequencies. For instance, 236 cm^{-1} is obtained for the $3sR$ state of C_2H_4 . Herzberg notes³, however, that presumably a strong anharmonicity should be taken into account. Merer and Schoonveld⁴ proposed such a potential function and for the $3sR$ state of C_2H_4 they calculated the ν_4 fundamental of 96 cm^{-1} . Summarizing, a possible value of the ν_4 fundamental can be within $250\text{--}100\text{ cm}^{-1}$.

In a study of inelastic neutron scattering (INS) on solid ZS, a vibrational transition of $185 \pm 5\text{ cm}^{-1}$ was detected. On the basis of Hiraishi's model of the complex, the authors²⁶ ascribed it to a torsion of ethene as a whole with respect to the rest of the anion. On the ground of the estimated interval $250\text{--}100\text{ cm}^{-1}$, however, we assign the 185 cm^{-1} transition to the searched fundamental of the (CC)*_{coord.} torsion, *i.e.*, to an "intra-ligand" torsion. It should be noted as a support that the vibrational selection rules for INS are not influenced by the symmetry restrictions for the activity in the Raman effect or IR absorption²⁷. Double this fundamental ($2 \cdot 185 = 370\text{ cm}^{-1}$) is lower than the observed first overtone (490 cm^{-1}) so that the difference $+120\text{ cm}^{-1}$ is in harmony with the prediction^{1,3,4} of a strong anharmonicity of ν_4 in the electronic excited states of free ethene (V and $3sR$).

If this assignment of ν_4 for ZS is correct, there are several serious subsequences. The above mentioned drastic changes in structure and bonding of coordinated ethene cause that one of its fundamentals (ν_4) drops into the interval of the fundamental PtCl_3 frequencies (below 350 cm^{-1}). From this it follows that in a normal coordinate analysis, the vibrations of PtCl_3 and of coordinated ethene cannot be treated separately, contrary to the reported studies^{10,12,14,19,20,28,29}. Conversely, couplings between the vibrations of PtCl_3 and ethene can reasonably be anticipated since the overall symmetry C_s of the Zeise's anion involves existence of only two symmetry types, A' and A'' .

Under these circumstances, the assignment of the CC torsional frequencies for fully deuterated ZS plays a substantial role. In free excited C_2D_4 , the mass of which is increased by 14.3% compared to C_2H_4 , the observed $2\nu_4$ is lowered from 468 to 286 cm^{-1} in the $3sR$ state⁴. In the case of $[\text{PtCl}_3(\text{C}_2\text{D}_4)]^{(-)}$, however, the deuterated ethene represents effectively small increase in mass of the whole anion so that the isotopic effect should be less pronounced than in the free species. Following this, we assign to the $2\nu_4$ frequency of coordinated C_2D_4 the band near 450 cm^{-1} (*cf.*

1-decene-1,2- d_x analogues¹⁵ of ZS: 568 cm^{-1} for d_0 and 519 cm^{-1} for d_3). The effect of changes in molecular weights (\downarrow) and of changes in the C=C bond order (\leftrightarrow) on the (CC)* torsion overtone $2\nu'_4$ of coordinated ethenes and in the free radical cations is visualized in the Scheme 2.



SCHEME 2

In free excited ethene in the $3sR$ state, a strong coupling is assumed¹ between the (C=C)* torsion and stretching vibrations: to twist the (C=C)* bond the energy must be also supplied to stretch the bond¹. The less pronounced shift of $2\nu'_4$ in coordinated C_2D_4 , compared to the free species, implies a very strong vibrational coupling between the ligand and PtCl_3 vibrations. This can be formulated in an extended form of the above assumption: to twist the (C=C)_{coord.} bond, the energy must also be supplied to stretch the (C=C)_{coord.} and Pt-ethene bonds simultaneously. Then, the isotopic ratios of the torsion $\tau(\text{C}=\text{C})_{\text{coord.}}^{\text{H}}/\tau(\text{C}=\text{C})_{\text{coord.}}^{\text{D}}$ and of the stretching vibrations $\nu(\text{C}=\text{C})_{\text{coord.}}^{\text{H}}/\nu(\text{C}=\text{C})_{\text{coord.}}^{\text{D}}$ and $\nu(\text{Pt}-\text{C}_2\text{H}_4)/\nu(\text{Pt}-\text{C}_2\text{D}_4)$ should be close, which is the case (Raman, aq. solution, from¹²): $492 \text{ cm}^{-1}/451 \text{ cm}^{-1} = 1.09$, $1241 \text{ cm}^{-1}/1353 \text{ cm}^{-1} = 0.92$, and $404 \text{ cm}^{-1}/387 \text{ cm}^{-1} = 1.04$, resp. The difference $1.09 - 0.92 = 0.17$ amounting to only 16% of the highest value, could be accounted for another coupling of ν'_2 with other vibrations, especially with the CH_2 in-phase scissoring mode ν'_3 (1522 and 961 cm^{-1} for coordinated C_2H_4 and C_2D_4 , resp.¹²).

In conclusion, the values of ν'_2 , ν'_3 , $2\nu'_4$, ν'_4 , and of the Pt-ethene stretching (plus the four C—H and the three Pt—(Cl,Br) stretching fundamentals) seem to be the only reliable frequencies of ZS which are presently known.

The assumed large amplitude of the (CC)_{coord.} torsion¹ presumably has an additional support in statements of Hamilton and coworkers⁹ about neutron diffraction crystallographic data⁹: "Poor crystal quality (of ZS) and high thermal motion have resulted in (structure) parameter variances considerably higher than usual in our laboratory... The standard deviations for positions and *r.m.s.* thermal amplitudes

vary from 0.01–0.02 Å for Pt and Cl to 0.03–0.06 Å for H." Although the poor crystal quality was accentuated⁹, it may be the enlarged amplitude of CH₂ twisting which is responsible for the observed effect.

Now, it is possible to summarize: The forward-donation of a π -electron from ethene to Pt is in many respects equivalent to promotions (or removal) of one π -electron in the free species by UV absorptions. The common features are: changes in the equilibrium geometry and potential function of the molecule manifested mainly in lowering the CC torsional and stretching frequencies and, moreover, in changes of vibrational couplings (ν_2' upward shifts). On this ground, we can con-

TABLE II
Main Characteristics of the Pt–Ethene Bond in Various Models of Zeise's Salt

Characteristics	Chatt–Duncanson ^a	Babushkin ^{16–19} –Hiraishi ¹²	Present work
Local el. state of ethene	ground-like	ground-like	excited-like
Hybridization of C atoms	sp^2 retained	mostly sp^3	sp^2
CC Bond order	somewhat less than 2	nearly 1	1.545 ^b
Number of bonding els. in CC	nearly 4	about 2	about 3
CC Bond length ((Å))	1.34	1.50	1.35–1.37 ^{c,d}
Orientation of CC to PtCl ₃	perpendicular	perpendicular	oblique ^c
Point symmetry of the anion	C_{2v}	C_{2v}	C_s^e
Local symmetry of ethene	D_{2h}	D_{2h} or C_{2v}	C_{2v}^d
Number of bonding els. in Pt–C ₂ H ₄	1–2 ^f	4 ^g	2
Ethene ligand	monodentate	bidentate ^g	monodentate
Coordination number of Pt	4	5	4
Symmetry of donation bonds	σ, π	σ, π	σ, σ
Predominating character	forward σ	back π	none, both equivalent
Character of C–H (above 3 000 cm ⁻¹)	olefinic	saturated strained ring	olefinic
CC stretching ν_2	1 516 ^h	1 243	1 243
CH ₂ scissoring ν_3	1 428 ^h	1 516	1 516
CC torsion ν_4	1 241 ^h	1 180	185 ⁱ
Main change in the IR spectrum	CC stretch. 1 623 → 1 516	CC stretch. 1 623 → 1 243	CC torsion 1 023 → 491 ^j

^a Ref.²⁴, the last review⁵². ^b Ref.²⁵. ^c Ref.⁸. ^d Ref.⁹. ^e The space group of symmetry of the crystal hydrate⁸ is $P2_1/c$ ($Z = 4$) which is isomorphous with C_{2h}^5 . ^f A different participation of the forward- and back-donations was assumed by various authors. ^g In PtC₂ ring. ^h Ref.⁵³. ⁱ According to the INS data²⁶, the assignment is ours. ^j The first overtone, $2\nu_4$.

clude: The local electronic state of coordinated ethene is comparable to some electronic excited states of the free species^{29,30}, although this local state need not be identical with any of the states known from the optical spectra of free ethene. As a consequence, the coordinated ethene represents an excited species with a very long life-time since the local excited state is preserved as long as the complex exists.

This new model for Pt–ethene bonding means the abandonment of the models by Chatt–Duncanson²⁴ and by Babushkin^{16–19} and Hiraishi¹² which all are surveyed in Table II. It is seen that the present model partially combines the best features of both older models in order to get a better fit with the experimental data. Although the basic difference is in the assumption of a local excited electronic state of ethene, there are some following inconsistencies in the model by Babushkin^{16–19} and Hiraishi¹².

TABLE III

The Experimental CC Bond Lengths r_{CC} (Å) in Free and “Bound” Ethene

Free ethene	r_{CC}	M ^a , ref.	“Bound” ethene	r_{CC}	M ^a , ref.
Ground state	$\left\{ \begin{array}{l} 1.333 \\ 1.338 \\ 1.339 \end{array} \right.$	(ED) ⁵⁴	Zeise’s salt	1.354	(ND) ⁹
		(IR) ⁵⁵		1.37	(XD) ⁸
		(Ra) ⁵⁶			
(3s) Rydberg	1.41	(UV) ⁴	Oxirane	1.47	(MW) ⁵⁸
1 st ionic	1.41	(est) ⁴	Azirane	1.48	(MW) ⁵⁹
V state	1.44–1.80	(est) ¹	Thiirane	1.49	(MW) ⁶⁰
T state	1.58	(est) ¹	Phosphirane	1.50	(MW) ⁶¹
(Ethane)	1.543	(IR) ⁵⁷			

^a M means method; ED electron diffraction, IR infrared, Ra Raman, UV ultraviolet, est estimated, ND neutron diffraction, XD X-ray diffraction, MW microwave.

Description of Vibrations and Terminology

With a non-linear polyatomic molecule, $3N-6$ normal vibrations are resolved to $N-2$ in-plane and $N-3$ out-of-plane deformations and to $N-1$ stretching vibrations³¹. For Zeises’s anion $N = 10$ so that the number of stretching vibrations is 9. These are $4 \times \text{C—H}$, $1 \times \text{CC}$, $3 \times \text{Pt—Cl}$, and $1 \times \text{Pt—ethene}$ only, not two. Let us assume for a moment that the PtC₂ ring is really formed in ZS. In such a three-atomic cyclic fragment ($3N-6 = 3$), there exists one and only vibration during which all the three bonds are stretched or contracted simultaneously. This mode is commonly

called the ring breathing vibration, the remaining two modes should be described as ring deformations. Therefore, such a notation as PtC_2 symmetric stretching, PtC_2 antisymmetric stretching, and simultaneously CC stretching (with different fundamental frequencies) is untenable as well as the PtC_2 rocking, wagging, and twisting which is familiar in the non-cyclic groups, *e.g.*, CH_2 .

Length of the CC Bond

Babushkin and coworkers¹⁶⁻¹⁸ and later Hiraishi¹² compared the coordinated ethene to ethylene oxide (oxirane). Appearance of the C—H stretching bands above 3000 cm^{-1} was pointed out¹²: "Although this is usually evidence that the carbon is unsaturated, it does not apply in the present case because a three-membered ring is one of the few exceptions to the rule that saturated C—H stretches are below 3000 cm^{-1} ". The statement implies that a change in carbon hybridization is considered, from the original sp^2 to nearly sp^3 . However, such a change is usually accompanied by lengthening of the CC bond (Table III). As it is seen, the crystallographic data^{8,9} for ZS speak against existence of the PtC_2 heterocyclic ring.

Geometry of the Anion of ZS

Under the assumption of C_{2v} symmetry for Zeise's anion¹², one stretching C—H mode would be of A_2 type, *i.e.*, infrared inactive. However, all the four C—H stretching bands are weakly observed in the IR spectrum of the solid^{10,12}. From this fact Grogan and Nakamoto¹⁰ concluded that the overall symmetry of the anion should be lower than C_{2v} . Recent X-ray diffraction data⁸ corroborate the lower point symmetry, C_s . In other words, there will be only two symmetry types of vibrations, A' and A'' . If the PtC_2 ring is formed in ZS then it lies in the only plane of symmetry and "both PtC_2 stretching vibrations" are of the same type, totally symmetrical A' .

Polarization of the Raman Lines near 400 and 490 cm^{-1}

A depolarization of the 492 cm^{-1} line was taken as a strong evidence for its assignment to the PtC_2 antisymmetric stretching vibration^{12-14,32} (B_1 for C_{2v}). However, it must be stressed here that the numerical value of the depolarization factor ρ was never published^{12-14,32}. As to this point, *e.g.*, for naturally polarized light, Herzberg states³¹: "It must be well understood that for the totally symmetric Raman lines ρ_n may be close to $6/7$, and therefore observation of $\rho_n = 6/7$ for a certain Raman line does not definitely exclude the possibility that it is totally symmetric". So, information conveyed by the term "depolarized" is misleading and even without the numerical value of ρ , it speaks neither *pro* nor *con* of the discussed models.

Number of Bonding Electrons Between Pt and Ethene

In alkyl derivatives of Pt with usual covalent bonding, the fundamental IR frequencies of Pt—C stretching vibrations occur in the $580-500\text{ cm}^{-1}$ region²⁰. Such σ -bonds are assumed to correspond to one electron bonding pair. Existence of the PtC₂ ring in ZS would represent formation of two such σ -bonds between Pt and the sp^3 -hybridized carbons so that "the two PtC₂ stretching fundamentals" near 400 and 490 cm^{-1} mean the use of approximately four bonding electrons in the coordination bond. This conclusion is incompatible with the structural parameters of the coordinated ethene (Tables II and III) and leads to the coordination number 5 for Pt. On the other hand, the forward- or back-donation bond alone would mean the one-electron bond or an ion pair which is contradictory to the fundamental frequency of about 450 cm^{-1} . Finally, "a ground-state combination" of both models, *i.e.*, retaining of the C=C double bond plus PtC₂ ring formation would lead to penta-valent carbon atoms.

DISCUSSION

It was the original idea of Mason³⁰ that distorted ligand geometries in so-called π -complexes of unsaturated organic molecules with transition metals resemble those of the free molecules in their electronic excited states. McWeeny and coworkers³³ detailed the idea as an implication of the models by Dewar³⁴ and Chatt-Duncanson²⁴: "In the complex the charge density is a weighted sum of densities associated with fragments in their various individual states. The terms in which the fragments are in their first excited triplet states appear with large weighting and all lead to a ligand charge distribution virtually identical with that possessed by an isolated ligand molecule in its first excited triplet state". In the general discussion to this point, Murrell said³⁵: "From a separate state theory, one is more likely to deduce that the ligand geometry is close to the geometry of the ligand excited singlet state or the ligand negative ion than that it is close to the triplet state geometry. As singlet and triplet states that are related will have similar geometries it is difficult to use the experimental data to differentiate these theories".

Firstly, the geometry of the coordinated ethene⁹ (local symmetry C_{2v}) speaks against the prevailing population of either π^* state for which, in the free molecule, the point group of symmetry D_{2d} is assumed¹. Moreover, the CC distance in the coordinated ethene^{8,9} does not support the idea of either π^* state, too. The arguments are indirect. In free ethene, the promotion of one electron from the HOMO to the (3s) Rydberg orbital lengthens⁴ the CC bond from 1.34 to 1.41 Å although the higher occupied orbital is essentially nonbonding with respect to the CC bond³. If the terminating level is the π^* antibonding orbital then a more pronounced change is expected¹. It is in contrast to the data^{8,9} for ZS in Table III. Furthermore, it is

seen from Table I that the values of ν_2' for ZS also throw doubt upon use of either π^* state as a model for the local excited electronic state of this ligand⁶. As a note, it may be questionable to differentiate between the singlet and triplet states of coordinated ethene at all since the spin-orbit coupling constant of Pt is two orders higher than that for C (4052 and 30 cm^{-1} , resp.³⁶; the $V-T$ separation in free ethene is¹ 3.0 eV, *i.e.*, about 24200 cm^{-1}). The X PES data for alkenic complexes of transition metals also do not support a significant participation of the antibonding ligand orbitals in the coordination bond³⁷. Finally, there exist additional circumstances which undermine the Chatt-Duncanson²⁴ model as well. These are photosensitized *cis-trans* isomerizations of free 2-butenes, assumed to proceed *via* the perpendicularly twisted C=C bond¹. The same mechanism is anticipated with 1,2-dideuterioethenes¹. In contrary to this, no isomerization was detected with 2-butenes either coordinated to Pt or released from the complexes^{38,39} (*cf.* also¹⁵).

For all these reasons, we abandon the Chatt-Duncanson²⁴ model of the " π -complexes", namely the concept of populating the π^* antibonding ligand orbital in the back-bonding with Pt. In other words, the electronic states of free alkenes resulting from this valence-shell transition cannot well serve as models for the ligands coordinated to Pt.

Let us turn our attention to geometries of ethene in complexes with various transition metals⁴⁰. Orientation of the CC bond with respect to the "coordination plane" of central atoms is generally oblique⁴⁰ and the angle ranges from 0° to 90°. In a back-donation bond, according to the older models^{24,34}, two lobes of a dp -hybridized orbital of a metal atom overlap the two corresponding lobes of the π^* antibonding orbital of ethene. A magnitude of the (+) overlap should be different from that of the (-) overlap to reach an oblique orientation of the CC bond. A possible explanation of the oblique orientation is in the prevailing population of higher levels of ethene, in the sense of orbitals more remoted spatially from the C_2H_4^+ core.

In the united atom orbital (UAO) approach these Rydberg MO's of ethene could be approximated¹ by the UAO's forming the (*ns*), (*np*), and (*nd*) series which precede the first ionization limit from π . For coordinated ethene, an extreme model of the first radical cation is less suitable because an ion pair $\text{Pt}^{(-)}\text{C}_2\text{H}_4^{(+)}$ can hardly be formed (the force constant¹⁰ 2.23 $\text{mdyn}/\text{\AA}$ is too high and the estimated²⁴ electric dipole moment of about 4 D is too low).

A Rydberg MO of free ethene of the type UAO (*ns*) can also be disregarded as the model because of different symmetries of the ethene⁹ coordinated in ZS (C_{2v}) and of the free species in the *nsR* states⁴ (D_2). By this elimination, there remain UAO's of the type (*np*) or (*nd*) since the others (*nf*, *etc.*) are too diffuse.

The Pt-ethene bond in ZS is nearly perpendicular⁸ to the CC bond of the ligand (84.2°), *i.e.*, it nearly coincides with the x -axis of free ethene (Scheme 1). The local electronic state of the coordinated ethene then can be regarded as an excited state of the free species after an electronic transition in the x -direction, say (np_x) $R \leftarrow N$

or $(nd_{x^2}) R \leftarrow N$. Under this assumption, it is possible to look for the cause of the oblique orientation of the CC bond with respect to the PtCl_3 plane. Only one of the two lobes of the UAO (np_x) or (nd_{x^2}) overlaps only one of the four lobes of a back-donating dp orbital of Pt. This implies that the back-donation bond formed also has a cylindrical σ symmetry as it has the forward-donation bond. Then, ZS in this approach is a σ, σ -complex and not a σ, π -, or simply, a π -complex. Since directional properties of a dp -hybridized orbital are dependent on the degree of mixing of d - and p -contributions, it is understandable why the midpoint of the CC bond lies outside the PtCl_3 plane⁸ and, consequently, why the PtCl bond opposite to the coordinated ethene is more ionic^{41,42} ($^{35}\text{Cl}-\text{NQR}$) and longer⁸ (2.327 Å) than both identical *trans*-PtCl bonds (2.305 Å).

Let us assume that the UAO of coordinated ethene, approximating a Rydberg MO in the free species, is the terminating orbital for both forward- and back-donated electrons between ethene and Pt. Under this assumption we get the electron pair forming the covalent bond between the ligand and central atom. Similar concept of covalent bonding in transition metal complexes was advanced by Nyholm⁴³: In a weak covalent bond unstable occupied orbitals at higher levels are used, leaving singly occupied orbitals at lower levels. It should be noted at this moment, that a MO description was shifted in the direction of VB terminology. Apparently, at least a three-center MO is formed around the Pt and C atoms since the calculation²⁵ revealed that also the chlorine orbitals are strongly mixed in the Pt-ethene bond in ZS. From this standpoint, the local electronic state of the coordinated ethene can be simulated either by the core of a doubly excited radical anion of free ethene (the bonding electron pair between Pt and ethene inclusive) or (without it) by the first radical cation of the free species in its ionic ground state⁶ plus the doubly excited $\text{Pt}^{(2-)}$ or $\text{PtCl}_3^{(2-)}$. Previously¹⁵, we chose the general term "a near-radical-cation".

Mason³⁰ stated that functions representing excited states of both the metal and ligand should be considered. This does not necessarily mean that a net energy must be supplied to reach local excited electronic states of both the fragments. According to the present model, whilst one direction of electron donation represents a descent in the electronic energy, the released energy is consumed by the complementary donation in the opposite direction. The overall interaction can be either endo- or exoergic. Presumably, some kind of intermolecular vibronic interactions may operate in this energetical stepwise cycle during the formation of ZS. Forms of the most active vibrations can be "read" directly from the geometry of Zeise's anion compared to the original configurations of free $\text{PtCl}_4^{(2-)}$ and C_2H_4 . From this point of view, it is of little value to speculate what kind of electron donation prevails because both the mechanisms are equally important.

Finally, a few unsolved problems should be mentioned: At present, there seems to be no indication of a local excited state of Pt or PtCl_3 in the vibrational spectra of ZS, *e.g.*, in the frequencies of the PtCl_3 stretching vibrations.

The $^1\text{H-NMR}$ spectra of ZS in solutions are interpreted in terms of practically free internal rotation around the Pt-ethene bond. Moreover, a rotation around the CC bond was postulated even in crystals of ZS (Part 2 of ref.²¹). However, drastic changes in structure and bonding of ethene after coordination should effect also the shielding of all its nuclei. So, the determined NMR quantities cannot be simply compared with data obtained for the free molecule in its electronic ground state.

Three of the four CH stretching bands of the coordinated ethene appear above 3000 cm^{-1} , however, their location does not prove plausibility of either model discussed here. An analogous situation is met in the IR spectra of ethene sorbed on supported metals⁴⁴. Without knowledge of the spectra in the lower wavenumber region, the absorptions above 3000 cm^{-1} prove neither associative nor dissociative chemisorption of ethene, nor participation of local excited electronic states proposed in this work.

An estimate of the barrier to torsion around the CC bond in the coordinated ethene is an important task. If ν_4' is not too hindered then it causes a mixing of vibrational and electronic states (*cf.* free ethene⁵) and the same holds for the (eventual) internal rotation around the Pt-ethene bond. Then, the crude approximation suggested here has to be refined, using permutation-inversion groups.

Whilst the first radical or the π^* states of free ethene represent only two extreme models of the local electronic state of this ligand, the Rydberg states offer a large variety of possibilities. Such an attempt for ethene coordinated to different transition metals will be the subject of a subsequent paper.

I am indebted to Dr V. Špirko, J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Science, Prague, for many valuable discussions.

Notes added in proof: With the aid of deuterated ethenes- d_1 , $-d_2$, and $-d_3$, it was proved⁴⁵ that the vibrational structure of the $V \leftarrow N$ transition in free species is connected mainly with the excited CC torsion ν_4' . The values of ν_2' frequencies are therefore unknown. Thus, one of the objections used against the singlet π^* state of the coordinated ethene becomes irrelevant (Table I), the other ones, however, remain effective.

The SCF $X\alpha$ -scattered wave method was used⁴⁶ to calculate the electronic structure of Zeise's anion, assuming C_{2v} symmetry of the square-planar configuration. It was found "that the back-bonding into the π^* ethylene orbital is rather less important than the σ -bonding, amounting perhaps to at most 25% of the total bonding of ethylene to Pt... The results therefore seem to indicate a strong bond formed between the metal and the olefin ligand mainly through a_1 orbitals. This is consistent with NMR studies which have indicated that the ethylene executes large amplitude rotational oscillations about the platinum-ethylene bond, thus suggesting that the π back-bonding cannot be very strong".

REFERENCES

1. Merer A. J., Mulliken R. S.: *Chem. Rev.* **69**, 639 (1969).
2. Duncan J. L., McKean D. C., Mallinson P. D.: *J. Mol. Spectrosc.* **45**, 221 (1973).
3. Herzberg G.: *Electronic Spectra and Molecular Structure of Polyatomic Molecules*, pp. 413, 533, 629. Van Nostrand, Reinhold, New York 1966.
4. Merer A. J., Schoonveld L.: *Can. J. Phys.* **47**, 1731 (1969).
5. Merer A. J., Watson J. K. G.: *J. Mol. Spectrosc.* **47**, 499 (1973).
6. Brundle C. R., Brown D. B.: *Spectrochim. Acta A* **27**, 2491 (1971).
7. McDiarmid R.: *J. Chem. Phys.* **55**, 2426 (1971).
8. Jarvis J. A. J., Kilbourn B. T., Owston P. G.: *Acta Crystallogr. B* **27**, 366 (1971).
9. Hamilton W. C., Klanderma K. A., Spratley R.: *Acta Crystallogr. A* **25**, S 172 (1969).
10. Grogan M. J., Nakamoto K.: *J. Amer. Chem. Soc.* **88**, 5454 (1966).
11. Grogan M. J., Nakamoto K.: *J. Amer. Chem. Soc.* **90**, 918 (1968).
12. Hiraishi J.: *Spectrochim. Acta A* **25**, 749 (1969).
13. Powell D. B., Scott J. G. V., Sheppard N.: *Spectrochim. Acta A* **28**, 327 (1972).
14. Hubert J., Kong P. C., Rochon F. D., Theophanides T.: *Can. J. Chem.* **50**, 1596 (1972).
15. Řeřicha R., Čapka M.: *This Journal* **39**, 2221 (1974).
16. Babushkin A. A., Gribov L. A., Gelman A. D.: *Dokl. Akad. Nauk SSSR* **123**, 461 (1958).
17. Hellman A. D., Babushkin A. A., Gribov L. A.: *Int. Conf. Coord. Chem., London, April 1959*. Spec. Publ. No 13, p. 116. Chem. Soc., London 1959.
18. Babushkin A. A., Gribov L. A., Gelman A. D.: *Russ. J. Inorg. Chem.* **4**, 695 (1959).
19. Gribov L. A., Gelman A. D.: *Zh. Strukt. Khim.* **2**, 569 (1961).
20. Adams D. M.: *Metal-Ligand and Related Vibrations*, p. 182, 208. Arnold, London 1967.
21. Herberhold M.: *Metal π -Complexes*, Vol. II: *Complexes with Mono-olefinic Ligands*, Part 1: *General Survey*. Elsevier, Amsterdam 1972; Part 2: *Specific Aspects*. Elsevier, Amsterdam 1974.
22. Maitlis P. M.: *The Organic Chemistry of Palladium*, Vol. I: *Metal Complexes*, p. 112, 123. Academic Press, New York 1971.
23. Hartley F. R.: *The Chemistry of Platinum and Palladium*, p. 381. Applied Science, London 1973.
24. Chatt J., Duncanson L. A.: *J. Chem. Soc.* **1953**, 2939.
25. Katô H.: *Bull. Chem. Soc. Jap.* **44**, 348 (1971).
26. Ghosh R. E., Waddington T. C., Wright C. J.: *J. Chem. Soc., Faraday Trans. II*, **69**, 275 (1973).
27. Hamilton W. C., Ibers J. A.: *Hydrogen Bonding in Solids*, p. 32. Benjamin, New York 1968.
28. Pradilla-Sorzano J., Fackler J. P., jr: *J. Mol. Spectrosc.* **22**, 80 (1967).
29. Smart C.: *Thesis*. London University 1962.
30. Mason R.: *Nature (London)* **217**, 543 (1968).
31. Herzberg G.: *Infrared and Raman Spectra of Polyatomic Molecules*, p. 90, 270. Van Nostrand, Princeton 1968.
32. Woodward L. A.: *Pure Appl. Chem.* **11**, 473 (1965).
33. McWeeny R., Mason R., Towl A. D. C.: *Discuss. Faraday Soc.* **47**, 20 (1969).
34. Dewar M. J. S.: *Bull. Soc. Chim. Fr.* **18**, C 79 (1951).
35. Murrell J. N.: *Discuss. Faraday Soc.* **47**, 59 (1969).
36. Griffith J. S.: *The Theory of Transition Metal Ions*, App. 6. Cambridge University Press, London 1971.
37. Mason R., Mingos D. M. P., Rucci G., Connor J. A.: *J. Chem. Soc., Dalton Trans.* **1972**, 1729.

38. Jonassen H. B., Kirsch W. B.: *J. Amer. Chem. Soc.* *79*, 1279 (1957).
39. Joy J. R., Orchin M.: *J. Amer. Chem. Soc.* *81*, 310 (1959).
40. Hartley F. R.: *Angew. Chem., Int. Ed. Engl.* *11*, 596 (1972).
41. Yesinowski J. P., Brown T. L.: *Inorg. Chem.* *10*, 1097 (1971).
42. Yesinowski J. P., Brown T. L.: *J. Mol. Struct.* *9*, 474 (1971).
43. Nyholm R. S.: *Quart. Rev. (London)* *3*, 340 (1949).
44. Little L. H., Kiselev A. V., Lygin V. I.: *Infrared Spectra of Adsorbed Species*, p. 100. Academic Press, London 1966.
45. Foo P. D., Innes K. K.: *J. Chem. Phys.* *60*, 4582 (1974).
46. Rösch N., Messmer R. P., Johnson K. H.: *J. Amer. Chem. Soc.* *96*, 3855 (1974).
47. Feldman T., Romanko J., Welsh H. L.: *Can. J. Phys.* *34*, 737 (1956).
48. Wilkinson P. G., Mulliken R. S.: *J. Chem. Phys.* *23*, 1895 (1955).
49. Reid C.: *J. Chem. Phys.* *18*, 1299 (1950).
50. Evans D. F.: *J. Chem. Soc.* *1960*, 1735.
51. Zelikoff M., Watanabe K.: *J. Opt. Soc. Amer.* *43*, 756 (1953).
52. Hartley F. R.: *Chem. Rev.* *69*, 799 (1969).
53. Powell D. B., Sheppard N.: *Spectrochim. Acta* *13*, 69 (1958).
54. Bartell L. S., Bonham R. A.: *J. Chem. Phys.* *31*, 400 (1959).
55. Smith W. L., Mills I. M.: *J. Chem. Phys.* *40*, 2095 (1964).
56. Dowling J. M., Stoicheff B. F.: *Can. J. Phys.* *37*, 703 (1959).
57. Hansen G. E., Dennison D.: *J. Chem. Phys.* *20*, 313 (1952).
58. Hirose C.: *Bull. Chem. Soc. Jap.* *47*, 1311 (1974).
59. Bak B., Skaarup S.: *J. Mol. Struct.* *10*, 385 (1971).
60. Shoemaker R. L., Flygare W. H.: *J. Amer. Chem. Soc.* *90*, 6263 (1968).
61. Bowers M. T., Beaudet R. A., Goldwhite H., Tang R.: *J. Amer. Chem. Soc.* *91*, 17 (1969).

Translated by the author.

ERRATA

RE-INTERPRETATION OF THE VIBRATIONAL SPECTRA OF ZEISE'S SALT. I. THE NATURE OF THE π -ETHENE BOND

R. ŘEŘIČHA

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In the previous paper¹ (This Journal 40, 2577 (1975)) 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..."

THE EFFECT OF THE CROSSLINKING OF ION EXCHANGERS ON THEIR CATALYTIC ACTIVITY FOR REESTERIFICATION

K. SETÍNEK

This Journal 42, 979 (1977).

In the Table II on p. 983 should be between the titles Liquid phase (cyclohexane) and Gas phase this line:

Reaction ^a	SS-2	SS-8	SS-15	SS-25	SS-50	P ^b
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