

COMPLEX FORMATION AND KINEMATIC COUPLING: $C_2H_4 \cdot PtCl_3^*$

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

Normal coordinate analyses including calculations of PED's were performed for $C_2H_4 \cdot PtCl_3$ system modelling Zeise's anion, $[(C_2H_4)PtCl_3]^-$. The wedgewise distortion of the C_2H_4 ligand known from the crystallographic data for Zeise's salt, was taken into account. Under these circumstances it was found that the kinematic couplings between the internal ligand and complex framework vibrational modes are rather small. The reliability of some existing assignments of the fundamental frequencies of Zeise's anion is discussed.

Zeise's salt, $K[(C_2H_4)PtCl_3] \cdot H_2O$, was the first organometallic compound synthesized by man¹ around 1830. Since 1950's, a huge amount of experimental data on this complex has been accumulated by various physical methods, however, sometimes with conflicting interpretations of the data. Studies of this stable complex can give information about a catalytically active particle $C_2H_4 \cdot PdCl_3$ predicted by analogy, the structure of which is not known for understandable reasons (cf. ref.²).

The electronic problem of the alkene-Pt(II) coordination bond can be attacked indirectly, using vibrational spectroscopy. On comparing the characteristic vibrational frequencies of the free and coordinated molecule of ethene, frequency shifts can be considered as an indirect measure of electronic changes of the ligand. However, an unambiguous assignment of the observed spectral bands of the complex to proper characteristic vibrations of C_2H_4 after its coordination remains to be a problem.

Moreover, it has been shown by calculations, e.g. ref.³, that some frequency shifts can result from other reasons than from changes in the potential energy of the C_2H_4 ligand. This phenomenon, entitled as the kinematic coupling effect³, results from non-vanishing off-diagonal inverse kinetic energy matrix elements which couple

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the internal ligand and complex framework modes (*CFM*). This has been demonstrated³ on a hypothetical molecule $C_2H_4.Tl.H_2O$, which is interesting from the point of view of catalysis by trivalent thallium, where the molecule of ethene has been considered in the planar configuration of nuclei.

On the other hand, a wedgewise distortion of coordinated C_2H_4 in stable Zeise's anion is known experimentally since 1970's from neutron⁴ and X-ray⁵ diffraction data. In our model calculations for $C_2H_4.PtCl_3$ complexed particle, eighteen diagonal **F** matrix elements (twelve for C_2H_4 and six for $PtCl_3$) were kept constant and the six remaining ones (the *CFM*'s) were varied in order to observe trends in eighteen corresponding frequencies and in potential energy distributions (*PED*'s).

The aim of this work was to compare the kinematic coupling effects for planar C_2H_4 in the thallic complex on one hand and the wedgewise distorted C_2H_4 complexed with the Pt(II) species on the other.

THEORETICAL

Calculations. All the calculations were performed on a UNIVAC computer of the Norwegian Institute of Technology in Trondheim, using the standard programs for normal coordinate analyses (cf. ref.³).

Symmetry coordinates of molecular vibrations. The idealized model of Zeise's anion belongs to the symmetry C_{2v} . When referring to the coordinate axes defined in Fig. 1, the normal vibrations are distributed into the various symmetry species as:

$$\Gamma_{vib} = 8a_1 + 4a_2 + 6b_1 + 6b_2 .$$

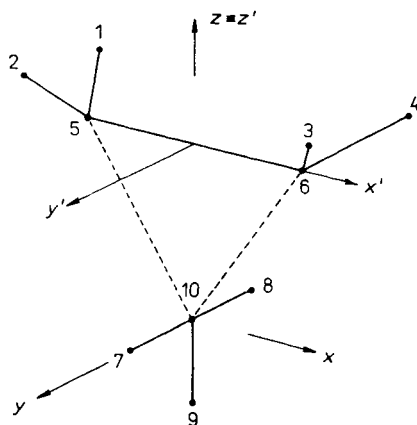


FIG. 1

The idealized geometry of Zeise's anion with the Kohlrausch-Herzberg orientation of x' , y' , and $z \equiv z'$ axes and C_{2v} symmetry. The bond lengths used (in pm): CH (108.7), CC (137.4), Pt-midpoint CC (203), Cl-Pt (234 for the atoms 9-10 and 230 for both 7-10 and 8-10); HCH (117°), wedge: angle of CH_2 planes (145°)

These modes of vibration may be divided into three types: the ethene vibrations, those of the PtCl_3 fragment, and the couplings between these two parts of the complex (*CFM*'s).

For C_2H_4 we have considered both the planar configuration of nuclei (symmetry D_{2h}), and the wedged distorted one which pertains to Zeise's anion in crystals (symmetry C_{2v} ; cf. Fig. 1). The correlation of the normal vibrations of these two configurations is given below, where the species of D_{2h} are denoted in parentheses (only here) by capital letters.

$$\Gamma_{\text{vib}}(\text{C}_2\text{H}_4) = 4a_1(3A_g + B_{1u}) + 3a_2(2B_{1g} + A_u) + \\ + 3b_1(B_{2g} + 2B_{3u}) + 2b_2(2B_{2u}).$$

In a preliminary set of calculations we used the symmetry coordinates for C_2H_4 from Cyvin and Cyvin^{6,7}. In the next round we wished to utilize the presumably best force field for free planar ethene due to Duncan and Hamilton⁸, where 116 experimental frequencies were used in the refinement of the force constants. Hence we executed the slight changes of the in-plane symmetry coordinates in order to conform the definitions of Duncan et al.⁸, adopted from Kuchitsu et al.⁹. These definitions imply unscaled bending coordinates.

For the part associated with the PtCl_3 fragment (cf. ref.¹⁰), which has the same symmetry (C_{2v}) as the whole complex, one obtains the following symmetry species:

$$\Gamma_{\text{vib}}(\text{PtCl}_3) = 3a_1 + b_1 + 2b_2.$$

For the whole complex there remain six vibrational modes which couple the internal ligand and complex framework modes (*CFM*). They are distributed into the symmetry species according to:

$$\Gamma_{\text{vib}}(\text{CFM}) = a_1 + a_2 + 2b_1 + 2b_2.$$

For the sake of simplicity of their description, these *CFM*'s can be characterized as the original translational (T'_x, T'_y, T'_z) and rotational (R'_x, R'_y, R'_z) degrees of freedom of the C_2H_4 molecule with respect to the original axis system $x', y', z \equiv z'$ (hence the primed quantities; cf. Fig. 1). These originally non-genuine vibrational degrees of freedom of the free C_2H_4 molecule are hindered in the field of PtCl_3 , and they become the genuine vibrational degrees of freedom of the whole complex.

For instance, the T_z mode represents the Pt-ethene stretching vibration, the other ones are deformation modes with the exception of R'_y , which can be regarded as another stretching mode with either a large force constant (the so-called antisymmetric PtC_2 ring stretching) or with a relatively small one (the so-called C_2H_4 pivoting or C_2H_4 tilting). We have studied both possibilities, the survey of which is given in Table I.

Precise definitions of the six coupling coordinates are given below:

$$\begin{aligned} a_1: T_z &= 2^{-1/2}(u_1 + u_2) \\ a_2: R_z &= (\eta_1 - \eta_2 + \eta_3 - \eta_4)/2 \\ b_1: T'_x &= 2^{-1/2}(\Theta_1 - \Theta_2) \\ R'_y &= 2^{-1/2}(u_1 - u_2) \\ b_2: T'_y &= (\eta_1 - \eta_2 - \eta_3 + \eta_4)/2 \\ R'_x &= (w_1 - w_2 - w_3 + w_4)/2. \end{aligned}$$

Here u designates the PtC stretchings, while the other symbols refer to bendings scaled by factors of the dimension of length in the usual way^{6,7}. Specifically, η and Θ pertain to the two types of CPtCl bending, where in the latter case (Θ) Cl stands for the unique (axial) Cl atom, and w pertains to HCPT angles.

The wedgewise distortion of C_2H_4 and its complexation with $PtCl_3$ requires a change in the notation of normal vibrations of the planar molecule which, however, will be used in the description of *PED*. For that reason, a correlation of both notations for planar and wedgewise distorted C_2H_4 is presented in Table II.

RESULTS AND DISCUSSION

The calculated frequencies are given in Table III together with the corresponding *PED*'s. In column 2, the notation for planar C_2H_4 is indicated (cf. Table II), in column 3 the frequencies for the free $PtCl_3$ fragment and the free wedgewise distorted C_2H_4 are collected.

The data for the $C_2H_4 \cdot PtCl_3$ complex are presented in column 4 for the case of the

TABLE I

The six complex framework modes (*CFM*) and their arbitrarily chosen force constants (in $\text{mdyn}/\text{\AA}$)^a for three types of interactions between C_2H_4 and $PtCl_3$

<i>CFM</i>	Interaction			R'_y	
	weak	moderate	strong	stretching ^b	deformation ^c
Stretching	0.10	0.20	1.00	R'_y, T_z	T_z
Deformation	0.01	0.05	0.10	R_z, T'_y, R'_x, T'_x	$R_z, T'_y, R'_x, T'_x, R'_y$

^a $1 \text{ mdyn}/\text{\AA} = 10^{-2} \text{ N/m}$; ^b the antisymmetric PtC_2 ring stretching (i.e., the coordination number 5); ^c i.e., the C_2H_4 pivoting or C_2H_4 tilting (and the coordination number 4).

strong interaction only (cf. Table I), which sufficiently illustrates the results of this study together with the additional Tables IV and V.

It is clear from these data that kinematic coupling effects in $C_2H_4 \cdot PtCl_3$ are relatively small, and on comparing them with the case of $C_2H_4 \cdot Ti \cdot H_2O$ they are smaller approximately by one order of magnitude. It is best illustrated by the CH_2 rocking vibration (b_{2u}), the shift of which for Tl^{3+} was $+157 \text{ cm}^{-1}$ whilst for $Pt(II)$ is $+24 \text{ cm}^{-1}$ only.

It follows from this fact that occasional large frequency shifts in the vibrational spectra of Zeise's anion must be attributed to changes in the potential energy of C_2H_4 after its coordination to $Pt(II)$. However, as it was stated above the problem is the unambiguous assignment of the observed spectral bands of the complex to proper characteristic vibrations of C_2H_4 after its coordination.

This problem can be well illustrated by two examples of different types of coordination of the ethene molecule to $Pt(0)$ or $Pt(II)$.

In case of a reaction between C_2H_4 and tetrakis(triphenylphosphine) platinum(0) with the coordination number 4, two phosphine ligands are replaced by one molecule of ethene.

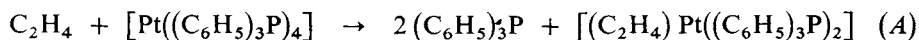


TABLE II

Correlation between the notations of some normal vibrations for planar and complexed wedge-wise distorted C_2H_4

Free planar $C_2H_4^a$	Complexed wedgewise $C_2H_4^b$
$T_z(b_{1u})$ rock. CH_2 (b_{1g})	$T_x(a_1)$: stretch. $Pt-C_2H_4$ twist. CH_2 (a_2)
CC torsion (a_u): twist. CH_2 $R_z(b_{1g})$	CC torsion (a_2): rock. CH_2 $R_x(a_2)$: hindered C_2H_4 rotation ^c
$R'_y(b_{2g})$ $T'_x(b_{3u})$ rock. CH_2 (b_{2u})	C_2H_4 pivoting or tilting (b_1) ^d $T_{CC}(b_1)$: o-o-p def. $C_2H_4-(PtCl_3)^e$ twist. CH_2 (b_2)
$T'_y(b_{2u})$ $R'_x(b_{3g})$	(b_2) : in-plane def. $C_2H_4-(PtCl_3)^f$ $R_{CC}(b_2)$: rock. CH_2^g

^a Axes: x' along the $C=C$ bond, y' , $z = z'$ (perpendicular to the original molecular plane, i.e., the symmetry species according to Kohlrausch¹⁶ and Herzberg¹⁷; ^b axes: x (parallel to x'), y (parallel to y'), $z = z'$, cf. Fig. 1; ^c also: PtC_2 twisting (ref.¹⁸) or C_2H_4 torsion (ref.¹⁹); ^d alternatively: the antisymmetric PtC_2 ring stretching (ref.¹⁸); ^e also: PtC_2 rocking (ref.¹⁸); ^f also: PtC_2 wagging (ref.¹⁸); ^g also: a barrelling motion (ref.¹⁹).

The reaction (A) indicates that the molecule of ethene behaves as a bidentate ligand which is accompanied by a marked lengthening of the CC bond from 133 to 143 pm after the coordination¹¹ (cf. 147 pm in the cyclic oxirane¹² C₂H₄O, and 149 pm in thiirane¹³). Thus, the assumption of a three-membered platinirane PtC₂ ring formation is substantiated in the Eq. (A) and, in this way, the original coordination number 4 is preserved for the central zerovalent Pt atom in the product.

TABLE III

Frequencies of the free wedgewise distorted C₂H₄, free planar PtCl₃, and complexed C₂H₄.PtCl₃ species (in cm⁻¹) and PED's

C ₂	Notation ^a	Free moieties (PED)	Complex, strong int. (PED)
8a ₁	CH stretch.	3 013 (99 + 1 CC)	3 014 (99 + 1 CC)
	CC stretch.	1 607 (63 + 36 sc)	1 611 (63 + 36 sc)
	sciss. CH ₂	1 350 (69 + 28 CC + 2 w)	1 351 (69 + 28 CC + 2 w)
	wag. CH ₂ (b _{1u})	923 (94 + 6 CC)	931 (91 + 7 CC + 2T ₂)
	ClPtCl str.	312 (58 + 42 PtCl)	324 (77 + 11 PtCl + 11T _z)
	PtCl stretch.	331 (59 + 41 PtCl ₂)	303 (60 + 23 PtCl ₂ + 16T _z)
	i-p def. ClPtCl T _z (stretch.)	151 (99)	149 (99 + 1T _z) 363 (69 + sec ^b)
4a ₂	CH stretch.	3 084 (100)	3 084 (100)
	rock. CH ₂ (b _{1g})	1 207 (95 + 5 tw)	1 212 (95 + 5 tw)
	twist. CH ₂	1 009 (95 + 5 r)	1 009 (95 + 5 r)
	R _z (def.)		131 (99)
6b ₁	CH stretch.	3 013 (100)	3 013 (100)
	sciss. CH ₂	1 429 (98 + 2 w)	1 430 (98 + 2 w)
	wag. CH ₂	929 (98 + 2 sc)	
	o-o-p def. ClPtCl	149 (100)	{sec Table IV and Table V
	R' _y (str. or def.) T' _y (def.)		
6b ₂	CH stretch.	3 104 (100)	3 105 (99)
	rock. CH ₂ (b _{2u})	824 (100)	848 (89 + 10R' _x + 1 CH)
	ClPtCl stretch.	319 (98 + 2 PtCl)	321 (96 + 2 PtCl + 2T' _y)
	i-p def. PtCl	198 (99 + 1 PtCl ₂)	211 (65 + 34T' _y)
	T' _y (def.)		171 (63 + 33 PtCl + 2 PtCl ₂)
	R' _x (def.)		567 (89 + 10 r)

^a Notation for planar C₂H₄; for changes cf. Table II; ^b 69T_z + 27ν(Pt-Cl) + 2 wag. CH₂ + 1(i-p) def. PtCl₂ + 1ν(PtCl₂).

TABLE IV
Extension of Table III for three interaction cases: R'_y is a stretching mode of $C_2H_4 \cdot PtCl_3$ complex (in cm^{-1} ; PED in %)

Notation (b_1 modes)	Free	Weak	Moderate	Strong
wag. CH_2 (b_{2g})	929	931 (98 + 2 sc)	934 (97 + 2 sc + $1R'_y$)	955 (93 + $6T'_x$ + 1 sc)
o-o-p def. ClPtCl	149	150 (98 + $1T'_x$)	159 (69 + $17T'_x$ + $14R'_y$)	135 (70 + $30T'_x$)
R'_y (str.) ^a		99 (98 + 1(oop) + $1T'_x$)	137 (80 + 19(oop))	307 (93 + 5 w + $1T'_x$)
T'_x (def.) ^a		51 (98 + 1(oop) + $1R'_y$)	108 (83 + 13(oop) + $4R'_y$)	176 (68 + 30(oop) + $1R'_y$)

^a For the force constants of R'_y and T'_x cf. Table I.

TABLE V
Extension of Table III for three interaction cases: R'_y is a deformation mode of $C_2H_4 \cdot PtCl_3$ complex (in cm^{-1} ; PED in %)

Notation (b_1 modes)	Free	Weak	Moderate	Strong
wag. CH_2 (b_{2g})	929	929 (98 + 2 sc)	930 (98 + 2 sc)	932 (98 + 2 sc)
o-o-p def. ClPtCl	149	150 (99 + $1T'_x$)	156 (84 + $16T'_x$)	135 (71 + $28T'_x$)
R'_y (def.) ^a		31 (99 + $1T'_x$)	69 (98 + $1T'_x$)	97 (98 + $1T'_x$)
T'_x (def.) ^a		51 (98 + 1(oop) + $1R'_y$)	110 (82 + 16(oop) + $1R'_y$)	180 (70 + 29(oop) + $1R'_y$)

^a For the force constants of R'_y and T'_x cf. Table I.

On the other hand, in the reaction between ethene and the PtCl_4^{2-} ion (in acidified aqueous solutions) only one chloride ligand is replaced by one molecule of ethene to form Zeise's anion, $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$. In this case the molecule of ethene behaves as a monodentate ligand preserving in Pt(II) species the coordination number 4 which is usual for the stable compounds of this type. It is accompanied by a relatively small lengthening of the CC bond of ethene from 133 to 137 pm after its coordination^{4,5}.

On the basis of these facts we believe that the assumption of the PtC_2 ring formation for Pt(0) in Eq. (A) is justified, and thus the R'_y mode may be the antisymmetric PtC_2 ring stretching vibration with a large force constant, generally $R'_y > T_z$.

On the other hand, the same assumption of the PtC_2 ring formation in Zeise's anion is not acceptable in view of the small increase in the CC bond length. Moreover, this assumption would mean an unusual coordination number 5 for this stable Pt(II) species. In other words, the R'_y mode in this case should be a mode with a relatively low frequency (the so-called C_2H_4 pivoting or tilting; generally $T_z > R'_y$; cf. refs^{14,15}).

This is a basic difference between two kinds of the molecular ethene ligand coordinated to two different stages of the Pt species, Pt(0) and Pt(II). Further studies of this problem seem to be warranted.

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