

IR SPECTRA OF DEUTERATED PROPENE ANALOGUES OF ZEISE'S SALT*

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The IR absorption spectra ($4000-250\text{ cm}^{-1}$) of anhydrous $\text{K}[(\text{propene})\text{PtCl}_3]$, using propene- $2-d_1$ and propene- $1,1-d_2$ as the ligands, were measured in KBr discs. A new weak band for the fundamental deformation frequency of the $\text{C}=\text{C}$ skeleton softened by the coordination of the propenes was found around 400 cm^{-1} , namely at 420, 417, and 375 cm^{-1} for d_0 , d_1 , and d_2 species, resp.. Vibrational couplings of the so-called $\nu(\text{C}=\text{C})$ with other modes of the ligands is discussed.

Alkene-Pt(II) coordination bond is an electronic problem. Its direct solution, *e.g.* by MO calculations, remains difficult because of its complexity. This problem can be attacked indirectly using vibrational spectroscopies. Characteristic bands, fundamental frequencies, and corresponding force constants can give some indirect evidence about the nature of the coordination bond. However, a correct assignment of an absorption band to one or another vibrational mode of an alkenic complex emerges as a new problem in both empirical and computational approaches.

The IR spectra of the propene analogue of Zeise's salt have been already measured¹⁻⁵, in one case also for the perdeuterated propene ligand³. The aim of papers¹⁻³ was to find a band for the fundamental stretching frequency of the $\text{C}=\text{C}$ bond of the propene ligand. A frequency shift of $\nu(\text{C}=\text{C})$ would be a quantitative measure of the propene-Pt(II) interaction, *i.e.*, of a $\text{C}=\text{C}$ bond softening in this particular case⁶. However, two different interpretations of the spectrum have been published. In the first^{1,3}, -9% shift of $\nu(\text{C}=\text{C})$ has been claimed (1653 cm^{-1} in gas $\rightarrow 1504\text{ cm}^{-1}$ in ligand) but -28% shift in the other² (from 1653 to 1188). These two interpretations represent quite different models of bonding in this complex: propene is thus either a monodentate or a bidentate ligand.

Since both models have been corroborated by normal coordinate analyses^{2,5,7,8} using ethene as the alkenic ligand, the controversy has remained unsettled. However, the fact that the so-called $\text{C}=\text{C}$ stretching vibration is not a pure vibrational mode but a coupled one further complicates the situation.

Efforts to extract a quantitative measure of the coordination from vibrational spectra are understandable. On the other hand, these efforts should not overshadow other aspects of the problem of the coordination bond. It has been already pointed out⁹ that molecular ligands in the coordination compounds are far from the electronic ground states corresponding to the free molecules. Changes in geometry and vibrational frequencies of these molecules after coordina-

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tion provide evidence of their activation⁹ due to the coordination bond. More specifically, this activation, within the framework of the electronic ground state of the whole complex, can be called a mutual chemical pseudoexcitation of the ligand and the transition element species.

The alkene-Pt(II) coordination bond causes also drastic changes in vibrational frequencies and geometry of molecules of the coordinated alkenes. According to refs^{10,11}, the vibrational frequencies of methylenes coordinated to PtCl_3^- are close to those of the positive ions of the free molecules known from UV photoelectron spectra (UPES). It has been shown¹¹ that the value of $\nu(\text{C}=\text{C})$ for the ionic ground state of free alkenes is not constant but depends on the number of methyl substituents of the $\text{C}=\text{C}$ bond. It ranges from 1 250 to 1 500 cm^{-1} (from ethene to 2,3-dimethyl-2-butene) and for the undeuterated propene the value of $\nu(\text{C}=\text{C})$ is $1\,370 \pm 30 \text{ cm}^{-1}$ (cf.^{11,15}).

The aim of this work was to estimate the vibrational coupling of $\nu(\text{C}=\text{C})$ with other vibrational modes of the ligand using partly deuterated $\text{CH}_3\text{CD}=\text{CH}_2$ and $\text{CH}_3\text{CH}=\text{CD}_2$ in the anhydrous $\text{K}[(\text{propene})\text{PtCl}_3]$ salts.

EXPERIMENTAL

Preparation of the compounds. 2-Deuteriopropene was prepared¹² by dehydration of 2-deuterioisopropanol (92.4% D; Inst. für physikalische Stofftrennung, Berlin, G.D.R.) at 300°C in a glass flow reactor on alumina (0.125–0.250 mm; Cat. No. R-10-11, BASF, F.R.G.). The dehydration of 2-deuterioisopropanol (20 mmol/h) was carried out in a stream of helium (600 mmol/h). The resulting water and unreacted isopropanol were removed from the gaseous phase at -40°C. The product was frozen off by liquid nitrogen and redistilled. The IR spectrum of gaseous 2-deuteriopropene was identical with that of the standard¹³.

1,1-Dideuteriopropene was prepared by a thermal decomposition of the deuterated n-propyltrimethylammonium hydroxide according to the standard procedure¹⁴. The starting 1-bromo-1,1-dideuteriopropene (7 g; 99% D; Inst. für physikalische Stofftrennung) was mixed with an ethanolic solution of trimethylamine (33 wt.%; 20 ml) and left to react for one week. Practically 100% conversion of the bromopropene to the hydroxide was attained (by GLC). The resulting reaction mixture was diluted with water until all crystals dissolved. The solution was shaken with freshly prepared silver oxide and, after filtration, it was distilled in a slow stream of helium. The IR spectrum of gaseous 1,1-dideuteriopropene was identical with that of the standard¹³.

Propene analogues of Zeise's salt were prepared from K_2PtCl_4 according to the standard method⁴. To check our procedure, the salt containing the undeuterated propene was prepared first. Its IR spectrum in KBr disc was in agreement with the published ones¹⁻⁵. The reactants were mixed in ampoules using the liquified propenes. The sealed ampoules were allowed to stand at room temperature over a weekend. A crystallization of the salts from aqueous solutions was carried out over solid KOH in an evacuated dessicator. The anhydrous salts were analysed for the K : Pt ratio and used for spectral measurements.

The vibrational spectra of the complexes. The IR spectra of anhydrous salts in KBr discs were measured on a grating spectrometer Perkin-Elmer, model 580. The accuracy of readings of the band maxima is about $\pm 1 \text{ cm}^{-1}$. As to the Raman spectra, the amount of the samples was not sufficient for measurements in our rotating sample holder. In a static arrangement, the complexes decomposed in both Ar^+ ion and He-Ne laser beams.

Penning ionization electron spectra (PIES) of the free propenes were measured on an instrument described earlier¹⁵. The ionization of the gaseous propenes was studied in the 0–12 eV interval, using metastable excited Ar atoms. As to the mono- or dideuteriopropene, their PIES were practically identical with that of the undeuterated propene¹⁵ (the first I.P. at about 9.74 eV) except the separation of maxima of the vibrational structure. This structure corresponds to excitations of the C=C stretching vibration in the ionic ground state ($v' = 0-5$). The separations of the first two levels ($v' = 0$ and $v' = 1$) were 1 370, 1 370, and 1 390 cm^{-1} for propene- d_0 , - d_1 , and - d_2 , resp., with an overall accuracy of $\pm 20 \text{ cm}^{-1}$. Owing to a relatively low signal-to-noise ratio, no additional vibrational structure was observed.

RESULTS

The IR absorption maxima of the deuterated propene analogues of Zeise's salt in KBr discs are listed below (in cm^{-1} ; intensity):

$\text{K}[(\text{CH}_3.\text{CD}=\text{CH}_2)\text{PtCl}_3]$: 3 068 m, 3 004 s, 2 963 s, doublet 2 925 w and 2 914 w, 2 860 w, 2 739 w, doublet 2 255 w and 2 245 w, 2 129 m, 2 015 w-br, 1 490 s and 1 470 sh, doublet 1 439 s and 1 421 m, 1 374 s, 1 346 m, 1 159 m, 1 054 s, doublet 1 022 s and 1 007 m, 929 w, doublet 904 s and 888 w, 831 s, 691 s, 486 w, 417 w-br, 383 m, 335 vs, 305 vs.

$\text{K}[(\text{CH}_3.\text{CH}=\text{CD}_2)\text{PtCl}_3]$: 3 024 m, 2 998 m, 2 962 m, 2 909 m, 2 860 w, 2 318 w, 2 195 w, 1 473 s, doublet 1 440 sh and 1 417 s, 1 370 s, 1 325 w, 1 255 w-br, 1 139 w, doublet 1 061 s and 1 045 sh, 1 003 w, doublet 960 sh and 951 m, 910 w, 889 s, 782 m, 756 m, 607 w, 471 w, 397 m, 375 w, 334 vs, 304 vs.

An IR absorption band with the maximum contribution of $\nu(\text{C}=\text{C})$ can be expected to appear around 1 400 cm^{-1} for the deuterated propene ligands. However, absorption bands belonging to the CH_3 deformations also appear in this region and it is necessary to identify them in the first place. This is done in Table I.

TABLE I

The IR absorption bands of the CH_3 deformation vibrations in the free and coordinated propenes (cm^{-1})

Def. CH_3	Propene- d_0		Propene- d_1		Propene- d_2	
	free ^a	coord.	free ^a	coord.	free ^a	coord.
$a'(\delta_a)$	1 459 ^b	1 450	1 453 ^c	1 440	1 453 ^d	1 440
$a''(\delta_a)$	1 442	1 430	1 443	1 420	1 450	1 415
$a'(\delta_s)$	1 378	1 363	1 390 ^c	1 375	1 382	1 370

^a Gas¹³. ^b 74% of $\delta_a(\text{CH}_3)$ + 17% of $\delta(\text{=CH}_2)$, both of a' symmetry. ^c 79% of $\delta_a(\text{CH}_3)$ + 13% of $\delta(\text{=CH}_2)$, both of a' symmetry. ^d 91% of $\delta_a(\text{CH}_3)$. ^e Including a combination frequency ($\nu_{19} + \nu_{20}$)¹³.

The bands remaining in the considered region are collected in Table II together with the data³ for the CD₃.CD=CD₂ ligand. They are assigned to the fundamental frequencies of the coupled $\nu(\text{C}=\text{C})$ and $=\text{CH}_2$ scissoring vibrations.

Previously¹⁶, we considered the 1 360 cm⁻¹ band of the undeuterated propene ligand as $\nu(\text{C}=\text{C})$ whereas the band at 1 390 cm⁻¹ was assigned by us to the CH₃ group. On the basis of the new results in Table I, we interchange the assignments of the two bands in order to preserve decreasing trends in the methyl deformation frequencies of all the three propene ligands. This change does not affect the qualitative conclusion that has been already presented¹⁶: The position of $\nu(\text{C}=\text{C})$ is variable for different methylenes coordinated to Pt(II) and for propene the $\nu(\text{C}=\text{C})$ band occurs at higher wavenumbers than that for the ethene ligand.

TABLE II

The IR absorption bands of the C=C stretching and =CH₂ scissoring coupled vibrations in the coordinated propenes (cm⁻¹)

Main contribution of	Propene ligand			
	<i>d</i> ₀	2- <i>d</i> ₁	1,1- <i>d</i> ₂	<i>d</i> ₆
$\delta(=\text{CH}_2 \text{ or } =\text{CD}_2)$	1 505	1 490	~ 1 000	~ 1 000
$\nu(\text{C}=\text{C})$	1 390	1 345	1 475	1 416

TABLE III

The IR absorption bands of the coordinated propenes in the 500--350 cm⁻¹ region

Tentative assignment	Propene ligands ^a		
	<i>d</i> ₀	2- <i>d</i> ₁	1,1- <i>d</i> ₂
$\nu(\text{Pt-propene})^b$	397 m	383 m	397 m
$\delta(\text{C}-\text{C}=\text{C})^c$	420 w ^d	417 w ^e	375 w ^f
$2\tau(\text{C}=\text{C})^{b,g}$	496 m	486 w	471 w

^a For propene-*d*₆ ligand observed³ at 370 cm⁻¹ with a medium intensity. ^b According to ref.⁵ the assignment can be interchanged. ^c A vibrational mode coupled with the CH₃ rocking vibration¹³. ^d Gas: 428 cm⁻¹ (86% + 18% rock. CH₃)¹³. ^e Gas: 422 cm⁻¹ (87%¹³). ^f Gas: 380 cm⁻¹ (83% + 14% rock. CH₃)¹³. ^g Probably coupled with the CH₃ torsion (the estimated fundamental frequency is at about 200 cm⁻¹).

According to refs^{4,5}, two medium intense bands have been observed for the propene ligand in the 500–350 cm^{-1} region. We observed another band in this region for all the three propene ligands studied here (Table III). We assign it to the deformation frequency of the C=C propene skeleton softened by the coordination to Pt(II). Up to now, this fundamental frequency has not yet been observed. Its appearance can be expected within the frequency limits given by “soft” and “hard” CCC skeletons of the free molecules of propane (369 cm^{-1} , ref.¹⁷) and propene (428 cm^{-1} , ref.¹³), respectively.

DISCUSSION

An indirect description of the alkene–Pt(II) coordination bond by means of vibrational data is complicated due to vibrational couplings of normal modes of the complex. However, such a vibrational coupling occurs already in the free molecules of alkenes and is changed after coordination. It is therefore useful to start the discussion with the free molecules of alkenes in their electronic ground state which implies a planar configuration of substituents around the C=C bond.

For C_2H_4 molecule, a coupling of the C=C stretching (ν_2) and the =CH₂ in-phase scissoring (ν_3) vibrations is proved¹⁸ by a non-zero value of the corresponding off-diagonal force constant in the 3×3 matrix (symmetry a_g). Even in the harmonic approximation the solution of this problem is not unique: There exist two sets of force constants reproducing well the ν_2 and ν_3 frequencies but representing quite different normal coordinates. The C=C bond stretching involves either a decrease of the HCH angle (a small contribution of ν_3 and a larger force constant $F_{\text{CC}} = 1\,090$ N/m) or involves an HCH angle widening (a large contribution of ν_3 and a smaller force constant $F_{\text{CC}} = 942$ N/m). A physically realistic set has been identified with the aid of ¹³C monosubstituted molecule of ethene: The C=C stretching vibration is strongly coupled with ν_3 , it is characterized by the smaller force constant, and a lengthening of the C=C bond widens the HCH angles. For this reason, a description of the C_2H_4 frequencies as the C=C stretching ($\nu_2 = 1\,623$ cm^{-1}) and =CH₂ in-phase scissoring ($\nu_3 = 1\,342$ cm^{-1}) modes is an oversimplification. In this connection, it is worth noting that this result represents an output of studies of 10 isotopomers of the ethene molecule in the years 1937–1981. In contrast, for ethene coordinated in Zeise's anion only two isotopomers were prepared.

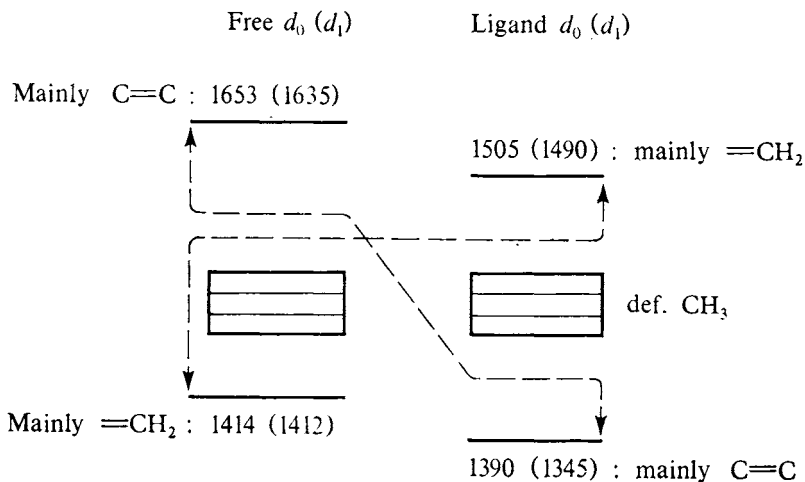
The case of this vibrational coupling in the free molecule of ethene is not unique. A strong coupling of $\nu(\text{C}=\text{C})$ and =CH₂ scissoring vibrations has been also proved in other molecules with the planar C=CH₂ grouping as allene or ketene¹⁹ and even in similar molecules as diazomethane or formaldehyde¹⁹.

With the free molecules of propenes containing the C=CH₂ grouping, the coupling of $\nu(\text{C}=\text{C})$ and =CH₂ scissoring modes is documented in Table IV by a calculated potential energy distribution¹³ (PED). It is clear that this coupling is further com-

plicated by contributions of other vibrational modes of the same symmetry (a') which is a consequence of a low point symmetry of the propene molecule (C_s).

Summarizing, the so-called C=C stretching and =CH₂ scissoring vibrations represent two different types of motion whose uncoupled frequencies lie close together¹⁹. After coordination, however, this condition is no more valid. A softening of the π bond by the interaction with Pt(II) lowers the frequency of $\nu(C=C)$ whereas the σ skeleton of the molecule is much less influenced. The C=C stretching and =CH₂ scissoring vibrations remain coupled in the ligand, however, to a much lesser degree than in the free molecules with the planar C=CH₂ grouping. Moreover, the coordination of propene to Pt(II) lowers the overall symmetry of the complex anion to the trivial one (C_1). It causes new couplings with other vibrational modes (originally of a'' symmetry), for instance with CH₃ deformations *etc.* (Tables I and II).

An illustration of the frequency shifts of the coupled C=C stretching and =CH₂ scissoring vibrations in the free and coordinated CH₃.CH=CH₂ and CH₃.CD=CH₂ (in parentheses) is on the common Scheme 1. Other relevant coupled vibrations are

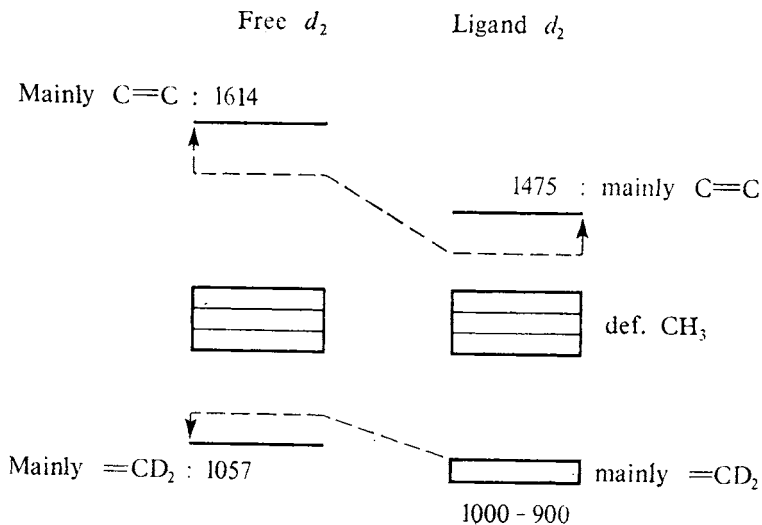


SCHEME 1

represented by a block denoted "CH₃ deformations" even though other modes can be involved. It is clear that $\nu(C=C)$ for both ligands appears at lower wavenumbers than this block of frequencies whereas the =CH₂ scissoring fundamental is well above it.

The relevant frequency shifts for the CH₃.CH=CD₂ ligand are on Scheme 2. Here the positions of $\nu(C=C)$ and =CD₂ scissoring frequencies are interchanged with respect to the "CH₃ deformations" block, *i.e.*, $\nu(C=C)$ for C=CD₂ ligand

is at a higher value than for the ligands with the $C=CH_2$ grouping. It represents an unusual isotopic shift of $\nu(C=C)$ but a similar one has been already observed for the coordinated ethene⁸. It has been explained by a change in the vibrational coupling of the idealized vibrational modes ν_2 and ν_3 after coordination of the mole-



SCHEME 2

TABLE IV

The potential energy distribution in free molecules of propenes in the electronic ground state^a

Propene	Exp. frequency (cm^{-1})	% Contribution of		
		$\nu(C=C)^b$	$\delta(=CH_2)^c$	Others
d_0	1 653	75	13	^d
	1 414	<10	65	19 of $\delta_a(CH_3)$
$2-d_1$	1 635	73	15	10 of $\nu(C-C)$
	1 412	<10	70	13 of $\delta_a(CH_3)$
$1,1-d_2$	1 614	67	<10	{ 11 of $\delta(=C-H)$
	1 057	<10	75	{ 10 of $\nu(C-C)$ ^d

^a Ref.¹³. ^b The stretching force constant is 901.5 N/m. ^c It denotes the $=CH_2$ or $=CD_2$ scissoring vibration. The force constant is 44.2 N/m. The force constant for the interaction between $\nu(C=C)$ and $\delta(=CH_2)$ is -22.2 N/m. ^d The remaining species of a' symmetry.

cule⁸. In our case of the propene ligands, this "upward shift" of $\nu(\text{C}=\text{C})$ is in a qualitative agreement with the observation of $\nu(\text{C}=\text{C})$ for the free positive ions of the propenes obtained by Penning ionization (*cf.* Experimental). Even though the PIES of the three propenes have been obtained at a relatively low resolution, $\nu(\text{C}=\text{C})$ of the heavier ion ($\text{CH}_3\text{CH}=\text{CD}_2^+$) has a higher value than those for the lighter ions with the $\text{C}=\text{CH}_2$ grouping.

On summarizing, the coordination of propenes to Pt(II) represents – from the point of view of vibrational spectroscopy – a more complicated case than that of $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$ because of symmetry. For Zeise's anion with an idealized C_{2v} symmetry, the block of the totally symmetric species (including $\nu(\text{C}=\text{C})$) contains 8 species only. In the case of the propene analogues with trivial C_1 symmetries, all the 33 vibrational modes are totally symmetric and therefore they can contribute, more or less, to all experimentally observed frequencies. On the other hand, a general feature in the coordination of alkenes to Pt(II) is preserved: The position of the $\nu(\text{C}=\text{C})$ band is not constant (at $1\,240\text{ cm}^{-1}$) but varies with the number of substituents on the $\text{C}=\text{C}$ bond.

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Note added in proof: The polarized UV absorption spectra of a single-crystal of Zeise's salt have been studied at 10K (Chang T. H., Zink J. I.: J. Amer. Chem. Soc. 106, 287 (1984)). It has been found that "the σ interaction between the olefin and the metal d orbitals is significantly more important than the π -interaction with the d orbitals". According to our opinion, it explains why the vibrational frequencies of the alkenic ligands of Pt(II) are similar to those of the free positive ions and not of the excited (π , π^*) states of the alkenes.