# VIBRONIC PROBLEMS IN 1-DECENE-1,2-d_x ANALOGS OF ZEISE'S SALT*

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The infrared absorption spectra ($10000-250\ cm^{-1}$) of anhydrous complexes of the type $K[PtCl_3(C_{10}H_{20-x}D_x)]$, $x = 0\text{-}3$, were measured in solid state. The seven 1-decenes-d_x stereo-specifically deuterated on the C=C bond solved the question of vibrational coupling between the C=C stretching and =CH_2 scissoring vibrations in these ligands. The spectra were interpreted as vibrational-electronic (vibronic) problems of the complex salt, the ligands of which being far from their ground electronic state. The vibrational bands of bonds of the ligands responsible for Pt-decene bonding were compared to the vibrational structures of radical-cations of propene known from the published electronic spectra. It is concluded that 1-decene-d_0 is bound to Pt-atom as a near-radical-cation species by one Pt ← decene σ-bond ($442\ cm^{-1}$), the band at $568\ cm^{-1}$ represents the first overtone of the vibronically excited (C=C)* torsion, and the (C=C)* stretching vibration is assigned to the band at $1397\ cm^{-1}$, whilst the =CH_2 scissoring mode is mainly characterized by the $1499\ cm^{-1}$ band. It is assumed that sp^2-hybridization of both carbon atoms is retained, however, the carbon–carbon bond order is reduced to nearly 1·5 due to the forward-donation bond, $Pt \leftarrow \overset{C}{\underset{C}{\|}}$.
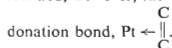
Alkenic complexes of transition metals had frequently been used as homogeneous catalysts, including Zeise's salt (further ZS), $K[PtCl_3(C_2H_4)]$. This species is considered the simplest model compound although the nature of Pt-alkene bond has not been generally established.

In the case of ZS, the number of bonds between Pt-atom and ethylene seems to be established by Hiraishi[1]. His interpretation of laser Raman spectrum of aqueous solution of ZS resulted in formulation of a three-membered, heterocyclic platinirane ring, PtC_2, with two Pt—C bonds originally proposed by Babushkin[2] and firstly "observed" in Raman spectrum by Ware[3,4]. The two strong Raman lines at 404 (polarized) and $492\ cm^{-1}$ (depolarized) were assigned[1,4] to the in-phase

and out-of-phase $Pt — \overset{C}{\underset{C}{|}}$ stretching vibrations of the ring, respectively. The formulation of the PtC_2 ring was supported by the Raman C—C stretching frequency[1] at $1241\ cm^{-1}$ (in ethane and ethylene at 923 and $1623\ cm^{-1}$, resp.). This interpretation has been confirmed several times[5,6]. The overall picture of bonding in ZS was based on changed carbon hybridization in the complex ($sp^2 \rightarrow sp^3$),[1,2] *i.e.* only alkene species in the ground electronic state were considered.

In the case of propene analog of ZS, the C=C stretching vibration was identified[7] with the strong band at $1504\ cm^{-1}$, however with respect to Hiraishi's results[1], this interpretation is

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doubtful because of possible interchange with the $=CH_2$ scissoring coupled vibration. The number of $Pt\overset{C}{-}C$ bonds is also uncertain because the Raman spectrum of the complex is not yet known. Furthermore, an answer from the sole IR spectrum is complicated by the fact that the solid monohydrate had been studied and the very strong and broad band of water near 500 cm^{-1} partially obscures the 500—400 cm^{-1} interval. So, only one medium intense band at 393 cm^{-1} came[7] into considerations. For instance, Chatt[7] has ascribed it to a torsion of propene with respect to the rest of the ion, *i.e.* no band for the stretching vibration of Pt-propene bond has been found[7]. The same conclusion was drawn by Powell (Table II in ref.[6]). Contrary to this, Nakamoto[8] interpreted the 393 cm^{-1} absorption as the band of one and only Pt-propene bond which generally should be in the 410—380 cm^{-1} region. As the last possibility, two Pt-propene bonds have been assumed by Adams[9]: "absorption at 393 cm^{-1} is due to $\nu(Pt-C_2)$, although the absence of a second band near 450 cm^{-1} is puzzling". In the re-measured spectrum of K[PtCl$_3$(C$_3$H$_6$)], a new medium IR band at 496 cm^{-1} was found[10] and assigned to the second searched $\nu(PtC_2)$ frequency. However, the ambiguity in the number of Pt—C bonds remained unsettled.

The aim of this work was to locate the C=C stretching band of coordinated 1-decene with the aid of species deuterated on the C=C bond and to determine the number of Pt-alkene bonds.

EXPERIMENTAL

1-Decene (BDH, England) was poured into an Al$_2$O$_3$ column and rectified under argon (b.p. 171°C). Its UV absorption spectrum (solution in cyclohexane, 1 cm cell) proved the absence of aldehydic compounds, the IR absorption spectrum was identical with the published one[11] and showed no isomeric decenes or water.

Deuterated 1-decenes (C$_{10}$H$_{20-x}$D$_x$, x = 1, 2, 3). The preparation of the seven species stereospecifically deuterated on the double bond has been described elsewhere[12] as well as the interpretation[13] of their IR absorption spectra[14]. Some of the samples were of different isotopic purity than previously reported[12-14].

Potassium trichloro(ethylene) platinite. Anhydrous ZS was prepared by a modified procedure[15] using an autoclave and 60 atm of ethylene. The reaction was complete overnight. Crystallization of the salt from aqueous solution was carried out in a vacuum dessicator over solid KOH. The crystalline product was dried and stored in the same manner. The IR spectrum in Nujol suspension or KBr-disc was identical with the published one[1]. The content of potassium was determined by flame emission (air–acetylene) at 766·5 nm by the method of calibration curves. For the anhydrous K[PtCl$_3$(C$_2$H$_4$)] it was found (10·5 ± 0·2) wt. % K, calc. 10·60.

Anhydrous potassium trichloro(1-decene) platinite (d$_0$). The 1-decene analog of ZS was prepared by a modified Anderson's[16] reaction (*1*)

$$K[PtCl_3(C_2H_4)] (s) + C_{10}H_{20} (l) \rightarrow K[PtCl_3(C_{10}H_{20})] (s) + C_2H_4 (g) . \qquad (1)$$

The preparation was tested in several solvents. Some of them, such as water, tetrahydrofuran, and to some extent water–ethanol, were found to be unsuitable, since they caused the reduction of Pt(II) and simultaneous formation of aldehydes from 1-decene. All the solvents, free of aldehydes (by UV), were degassed and all manipulations with samples were carried out under argon.

TABLE I

IR Spectra of 1-Alkene-d_0 Analogs of Zeise's Salt (cm^{-1})[a]

Propene[b]	Propene[c,d]	1-Decene[e]	Assignment[f]
		The Bands Relevant to the Problem of a Coordination Bond	
3 068 m	3 071	3 074 w	stretching =C—H
3 034 m	N.O.	3 019 sh	
3 010 m	3 012	3 001 sh	
N.O.	2 033	2 025 vw	2x wagging =CH$_2$
1 504 s	1 504 s	1 499 m	(sciss. =CH$_2$) + stretch. (C=C)*
1 365 s	1 361 s	1 397 m	stretch. (C=C)* + sciss. =CH$_2$
N.O.	1 299 m	1 282 w	
1 252 vw	N.O.	1 251 w	
1 175 w	1 188 m	1 187 w	
1 010 m	1 014 s	1 009 m	wagging =CH$_2$ (doublet due to crystal field[1])
990 m	994 s	993 m	
932 m	932 s	928 w	stretching =C—C
830 w	887 w	859 w	
809 w	804 s	818 w	
635 vw	N.M.	N.O.	
N.O.	496 m	568 w	2x torsion (C=C)* or 2x twist. =CH$_2$ (N 575 m)
393 m	397 m	442 m	stretching Pt-alkene (CD$_3$: 370 m)
N.M.	194 m	N.M.	? torsion (C=C)* or twist. =CH$_2$
		The Bands Irrelevant to the Problem of a Coordination Bond	
2 971 sh	2 967	2 960 s	stretching CH$_3$ or (CH$_2$)$_7$ (CD$_3$: 2 203 sh,
2 965 m	2 954	2 925 vs	2 208 vw)
2 911 vw	N.O.	N.O.	
—	—	2 873 sh	
—	—	2 855 s	
1 621 vs	1 645	1 620 m	deformation H$_2$O
—	—	1 466 s	scissoring (CH$_2$)$_7$
1 449 s	1 447 s	1 457 sh	antisym. def. CH$_3$[g]
1 429 s	1 431 s	1 438 sh	(CD$_3$: 1 048 m, 1 038 m)
1 392 m	1 395 s	1 378 m	sym. def. CH$_3$[g] (CD$_3$: 864 vs)
—	—	1 340 vw	twisting (CH$_2$)$_7$[g]
—	—	1 301 vw	wagging (CH$_2$)$_7$[g]
—	—	1 120 w	rock. CH$_3$ + stretch. (C—C)$_8$[g]
1 049 s	1 055 s	1 038 w	rock. CH$_3$ (CD$_3$: 762 m)
—	—	979 sh	stretching (C—C)$_8$[g]
—	—	722 m	rocking (CH$_2$)$_7$[g]
530 vs, br	—	510 m	rocking H$_2$O

TABLE I
(Continued)

Propene[b]	Propene[c,d]	1-Decene[e]	Assignment[f]
330 vs	337 vs	330 vs	} stretching PtCl$_3$
N.O.	327 sh	N.O.	
306 vs	306 vs	305 vs	
N.M.	247 m	N.M.	
N.M.	156 m	N.M.	
N.M.	98 m, br	N.M.	} lattice vibrations
N.M.	75 w, br	N.M.	

[a] Meaning of abbreviations: w — weak, m — medium, s — strong, v — very, sh — shoulder, br — broad, N.O. — not observed, N.M. — not measured. [b] Monohydrate in Nujol[19]. [c] 3 500 to 700 cm^{-1}, monohydrate in Nujol[18]. [d] 550—33 cm^{-1}, anhydrous (?) in Nujol[10]. [e] This work, anhydrous in KCl-disc. [f] The (+) sign means coupled vibrations. The bond marked with an asterisk means an electronically excited bond. The mark 2x means the first overtone. The bands for CD$_3$ in parentheses are for K[PtCl$_3$(C$_3$D$_6$)] . H$_2$O, ref.[19] [g] Ref.[30].

At least a twofold excess of 1-decene was necessary for the reaction (1) to proceed quantitatively. However, as only amounts bellow 0·1 ml of the deuterated species were available, any further manipulation with products would be difficult. Therefore, the reaction with 1-decene was carried out in diethyl ether saturated with KCl, which also prevented the formation of Zeise's dimer:

$$[PtCl_2(C_{10}H_{20})]_2 + 2 KCl \rightarrow 2 K[PtCl_3(C_{10}H_{20})]. \qquad (2)$$
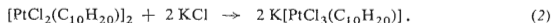
The pale yellow mixture of KCl and the product remaining after evacuation of volatile components was used for spectral measurements. The typical procedure was following.

Anhydrous potassium trichloro(1-decene-d$_x$) platinites, K[PtCl$_3$(C$_{10}$H$_{20-x}$D$_x$)], $x = 1-3$ (I—VII). An anhydrous ZS powder (75 mg, 0·2 mmol), placed in a glass ampoule, was mixed with 35 ml of the diethyl ether saturated at 25°C with KCl, then 0·095 ml (0·5 mmol) of 1-decene-d$_x$ was added. The reaction mixture was homogenized by adding 8 ml of ethanol (96%) and stirred under argon for 1 hour at room temperature. Then, the volatile components were removed under vacuum, such that temperature did not exceed 20°C. The product was then dried under high vacuum for several hours. Finally, the ampoules were filled with argon and stored in a dessicator with KOH.

The whole procedure was repeated with KCl only, the resulting "blank-KCl" served as the reference standard for the IR measurements.

Spectral Measurements

The products were handled in a dry-box flushed with dried nitrogen. They were mixed with additional KCl (BDH, purity "standard for atomic absorption spectroscopy"), homogenized, and pressed in an evacuated die (i.d. 2 cm, 36 tons). The quality of the products was checked by IR spectra of the discs.

First of all, the absorption bands of the starting materials (solvents, ZS, and free 1-decene-d_x) were looked for ($1100-600$ cm^{-1}) but not found. Then the eventual by-product, Zeise's dimer, was semi-quantitatively determined near 360 cm^{-1} (cf.[1]). If any, the amounts of it were estimated to be always bellow 5 wt. %. The spectra of the KCl-discs were then recorded in the near and middle IR regions ($10000-300$ cm^{-1}), using the blank-KCl-disc in the reference beam.

To check the position of bands of adsorbed moisture on the KCl-discs, the products were measured as the suspensions in Nujol ($4000-250$ cm^{-1}). After dilution with additional Nujol, these suspensions were used as films between SiO$_2$ windows for recording the electronic spectra of the samples in the $50000-10000$ cm^{-1} region. These spectra revealed only UV absorptions of the shape of a diffusion-controlled polarographic wave. The midpoint of the "wave" was taken as a measure of absorption wavelength. In all cases of the coordinated 1-decenes-d_x ($x =$ $= 0-3$) it was equal to 314 $\pm$ 2 nm whilst for the starting ZS being at 283 nm.

As to the IR spectra, it is noteworthy that the absorption bands of n-octyl group in 1-decenes-d_x were practically identical with those of Nujol. Generally, the suspensions offered worse developed spectra than the pressed KCl-discs. The bands of mulls were broader, shifts up to 10 cm^{-1} were observed, however, the overall pattern of the spectra was retained.

Before any interpretation of the IR spectra, the absorption bands of deuterium-impurities d_0, I, III, and V (cf. List of frequencies) in the samples were identified together with the weak bands of n-octyl group[17].

Owing to a high fluorescence, the pressed products gave no reasonable laser Raman spectra.

Instruments

Two double-beam Beckman spectrometers were used for the measurements: model DK-2A (SiO$_2$-prism, $50000-3000$ cm^{-1}) and IR-7 (NaCl- or CsI-prism/grating, $4000-250$ cm^{-1}). The instruments were calibrated with the respective wavenumber standards: Holmium Oxide or Didym Glasses and a polystyrene film. The accuracy of readings was about $\pm$ 2 cm^{-1}.

RESULTS

The fingerprint IR spectra of the propene analog of ZS, K $\left[\text{PtCl}_3(\text{C}_3\text{H}_6) \right]$. H$_2$O, had been reported in two papers[7,18]. Moreover, the propene-d_6 analog had been investigated[19], however, all the three spectra have remained mostly unassigned. We partially interpret these results and compare them to our 1-decene-d_0 analog in the first part of Table I. The second part of the table contains the bands irrelevant to the problem of a coordination bond, i.e. it contains the bands of the alkyl group (methyl in propene, n-octyl in 1-decenes-d_x), of adsorbed moisture, and of PtCl$_3$ moiety. These bands are common to all the deuterated samples, K $\left[\text{PtCl}_3(\text{C}_{10}\text{H}_{20-x}\text{D}_x) \right]$, $x = 1-3$ ($I - VII$), and will be omitted in the corresponding List of frequencies relevant to a coordination bond.

The 1-decenes-d_x in complexes $I - VII$ are specified by deuterium atom positions on C=C bond, by the deuterium-atom-position purity in mole %, by roman numeral of an eventual impurity, and by the analytical bands[13] of the free ligand in liquid state. The free C=C stretching frequency is also accompanied by its absorbance (in parentheses) at the cell thickness 0·00183 cm, cf.[13,17]. All numbers are in cm^{-1}

and refer to KCl-discs except those designated N (in Nujol). Intensities of the bands were classified with respect to the strong absorptions by n-octyl group so that most of them are weak, the stronger ones are denoted by the bold letters **m**, **s**. Compound *II* has the weakest spectrum of the series *I* – *VII* because the starting decene had been available in half amount than with the other cases (only 0·045 ml).

A direct comparison in a table between the coordinated $D_3C . DC = CD_2$ and the 1-decene-d_3 analog (*VII*) is impossible because of different vibrational behaviour of CD_3 group and n-octyl group. So, the interpretation needs some comment as it is the basis for our assignment of 1-decene-d_x analogs.

We start with the assignment[20,21] of the vibrational fundamentals for free molecules of C_3H_6 and C_3D_6. In the case of C_3H_6 there exist the four frequencies in the 1 600 to 1 350 cm^{-1} region[21]: scissoring $=CH_2$ (1 499 cm^{-1}), two antisymmetrical CH_3 deformations (1 460, 1 449 cm^{-1}), and symmetrical CH_3 deformation (1 381 cm^{-1}). The IR spectrum of the C_3H_6 analog of ZS contains[7] a progression of the five medium-to-strong bands at 1 504, 1 449, 1 429, 1 392, and 1 365 cm^{-1}, the first four of them correspond to the above mentioned vibrations. Bands corresponding to these vibrations in free C_3D_6 must shift to lower wavenumbers between 1 200 – 900 cm^{-1}.

TABLE II

The IR Bands of the (C=C)* Stretching and (=CH_2, =CHD, =CD_2) Scissoring Vibrations in 1-Decene-d_x Analogs of Zeise's Salt (cm^{-1})

End group	C^a	Free[b] ν(C=C)	Bound ν(C=C)*	$\Delta\nu^c$ (C=C)	$\Delta\nu^c$ in %	Free[d] sciss.	Bound sciss.	Δ^c sciss.	Δ^c in %
=CH_2	d_0	1 642	1 397	−245	−14·9	1 413	1 499	+86	+6·1
	I	1 625	1 366	−259	−15·9	1 402	1 487	+85	+6·1
	II	1 622	?[e]	?	?	1 230[f]	?[e]	?	?
	III	1 619	1 443	−176	−10·9	1 230[f]	1 338	+110	+9
=CHD	*IV*	1 604	1 439	−165	−10·3	1 266[g]	1 342	+76	+5·7
	V	1 596	1 436	−160	−10·0	1 253[g]	1 327	+74	+5·9
=CD	*VI*	1 601	1 442	−159	− 9·9	1 053	1 120	+67	+6·4
	VII	1 583	1 415	−168	−10·6	1 046	1 100	+54	+5·2
=CH_2^h	d_0	1 642	1 499	−143	− 8·7	1 413	1 397	−16	−1·1
	I	1 625	1 487	−138	−8·5	1 402	1 366	−36	−2·6

[a] Compound, cf. List of frequencies. [b] Wavenumbers for free liquids[13]. [c] The difference $\Delta\nu$ (bound-free) in per cent of the corresponding "free" value. [d] Wavenumbers for free d_0, *I*, *VI*, *VII*; the others see [f,g]. [e] Not found. The weakest spectrum, see Experimental. [f] Approximate values; directly read from the published[31] spectra of gaseous propenes-1-d_1. [g] Values[32] for gaseous vinyl chlorides-1,2-d_2. [h] Interpretation after Powell[6] : the values of the "bound" (C=C)* stretching and =CH_2 scissoring are interchanged.

The spectrum[19] of the coordinated C_3D_6 reveals the only band at 1416 cm^{-1} in the 1600—1350 cm^{-1} region. The bands at 1365 cm^{-1} (C_3H_6-ZS) and 1416 cm^{-1} (C_3D_6-ZS) correspond to the (C=C)* stretching vibrations of the coordinated propene-d_0 and -d_6. An upward shift (1365 → 1416 cm^{-1}) after deuteration and coordination has been already observed by Hiraishi[1] in the case of ethylene-d_0 and -d_4 (1241 → 1353 cm^{-1}). It has been explained[1] by loosening of vibrational coupling between the =CH$_2$ scissoring and C=C stretching vibrations due to the deuterium isotopic substitution and coordination. A similar upward shift after ionization of free C_2H_4 and C_2D_4 has been also observed in their photoelectron spectra (1290 → → 1370 cm^{-1}) (ref.[22]).

List of Relevant IR Frequencies of Complexes *I — VII* (cm^{-1})

I (2-d_1; 94·5 mol %; impurity: d_0; free: 3079, 2222, 1625 (0·37), 909, 842): 3075 w, 3011 sh, 2243 w, 1487 **m**, 1366 **m**, 1041 w, doublet 1010 **m** and 994 **m**, 898 w-br, 543 **m** (N 537 **m**), 437 **m**.

II (trans-1-d_1; 81·6 mol %; impurity: d_0; free: 3033, 3000, 2267, 1622 (0·26), 978): 3 027 sh, 3009 w, 2262 vw, 1327 w, 1250 w, 1036 w, doublet 947 **m** and 933 **m**, 922 sh, 894 w-br, 858 w, 749 w, 655 w, 568 **m** (N 574 **m**), 428 **m**.

III (cis-1-d_1; 99.3 mol %; impurity: d_0; free: 3054, 3013, 2250, 1619 (0·19), 799): 3032 sh, 3009 w, 2240 vw, 1443 w, 1338 **m** 1320 w, 1249 w, 1213 w, 1199 w-br, 1035 w, 1016 w, 964 **m**, 923 w, 913 w, 894 w, 828 w, 753 w-br, 700 **m**, 549 **m** (N 559 **m**), 431 **m**.

IV (cis-1,2-d_2; 72·6 mol %; impurity: *I*; free: 3030, 2274, 2222, 1604 (0·27), 878): 3030 w, 2262 vw, 2227 **m**, 1439 **m**, 1400 w, 1277 w-br, 1192 w, 1081 w, 1042 w, 964 w, 849 w, 791 **m**, 637 w, 540 **m** (N 537 **m**), 417 **m**.

V (trans-1,2-d_2; 95·7 mol %; impurity: *III*; free: 3052, 2251, 2222, 1596 (0·15), 881, 716): 3030 w, 2265 vw, 2240 w, 1437 **m**, 1327 w, 1280 **m**, 1250 w, 1210 w, 1138 w, 1044 w, 983 w, doublet 945 **s** and 934 sh, 891 w, 810 w, 750 w, 740 w, doublet 695 **m** and 686 sh, 517 **m** (N 531 **m**), 429 **m**.

VI (1,1-d_2; 77·3 mol % impurity: *III*; free: 2 999, 2302, 2213, 1601 (0·19), 725): 3008 w, 2320 w, 2196 w, 1442 **m**, 1247 w, 1208 w, 1120 **m**, 1075 w, 1036 w, 1005 w, 964 w, 893 w, 858 w, 780 **m**, 761 **m**, 622 w, 546 **m** (N 556 **m**), 423 **m**.

VII (1,1,2-d_3; 80·5 mol %; impurity: *V*; free: ((2249, 2223), 2202, 1583 (0·21), 711): 2232 w, 1415 **m**, 1281 w, 1200 vw, 1154 w-br, 1100 **m**, 1043 vw, 1020 w-br, 977 w-br, 941 w-br, 892 w, 850 w-br, doublet 795 **s** and 765 sh, 612 **m**, 519 **m** (N 526 **m**), 412 **m**.

For this reason, we focused our attention to the assignment of the C=C stretching vibration originally coupled with the =CH$_2$ scissoring mode. In some cases (*III — VI*), we found the (C=C)* band superimposed on the complex absorption by n-octyl group

(*cf.* second part of Table I). The band was always well resolved and relatively prominent. The results are summarized in Table II. The last row, repeatedly denoted $=CH_2^h$, represents an alternative assignment proposed by Powell and coworkers[6] in which both frequencies are interchanged. However, the resulting $(-)$ sign of the percentual shift of the $=CH_2$ scissoring frequency is out of trend in the whole series, so we reject this kind of assignment.

After coordination of the 1-decenes-d_x in ZS, two vibrational counteracting effects could be deduced from the position of the $(C=C)^*$ band. To illustrate these effects, Fig. 1 is presented. The deuterium substitution in the position 2 led to a downward
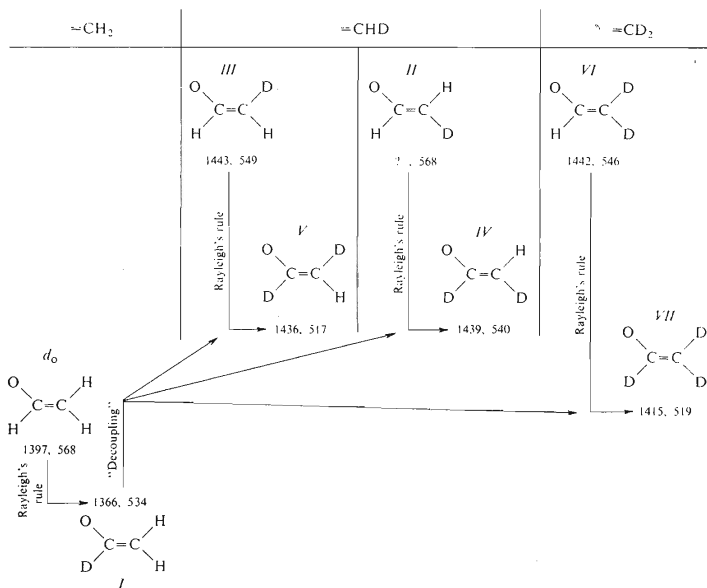
FIG. 1

The Two IR Bands (cm^{-1}) of the Vibronically Excited $(C=C)^*$ Bond in 1-Decene -d_x Analogs (d_0, *I—VII*) of Anhydrous Zeise's Salt in KCl-Discs

O means n-octyl group.

shift in accordance with the simplest Rayleigh's isotopic rule (case $d_0 \to I$). A deuterium mono- or disubstitution in the position 1 (i.e. =CHD, =CDH, =CD$_2$) led to "a vibrational decoupling" between the original ν(C=C) and scissoring =CH$_2$. So, the "1-deuterium-induced decoupling" caused ν(C=C)* to be shifted to higher wavenumbers (cases $II - VII$) compared to the case d_0 or I. If the 1-deuterium substitutions were accompanied by the deuteration in the position 2, the isotopic down--shift was observed besides the decoupling which prevailed (cases $III \to V$, $VI \to VII$).

It is noteworthy that the isotopic down-shift due to the 2-deuteration was obeyed by another band in the $570 - 515$ cm^{-1} interval which is also involved in the Fig. 1.

Fig. 2

A Comparison of the (C=C)* Stretching and Torsion Vibrations (cm^{-1}) of Propene Excited According to Franck-Condon's Principle or by Coordination (with the coordinated species above, the sign for negative charge of anions is missing)

This band enabled the proper location of compound *II* in Fig. 1 although the (C=C)* stretching frequency was not found in that case. We ascribed the band to the first overtone of the vibronically excited (C=C)* torsion (or =CH_2 twisting) in accordance with the high resolution UV absorption spectrum[23] of propene-d_0 where it has been found on the absorption continuum as a vibrational structure with a spacing of 527 cm^{-1}. We point out here that the band in Nujol mulls of the samples d_0, *I — VII* was found to be strongly "solvent-dependent" (KCl *vs* Nujol, *cf.* List of frequencies and ref.[8]).

There was another band in the 445—410 cm^{-1} region of the series d_0, *I — VII* which exhibited normal deuterium isotopic shift as it is seen from the following trend (KCl, in cm^{-1}): 442 (d_0), 437 (*I*, d_1), 431 (*III*, d_1), 428 (*II*, d_1) 429 (*V*, d_2) 423 (*VI*, d_2), 417 (*IV*, d_2) and 412 (*VII*, d_3).

We assigned it to the stretching vibration of one Pt-decene σ-bond in accordance with Nakamoto[8].

With the remaining IR bands the effect of deuterium substitutions was not so clear. The wagging vibration of =CH_2, =CHD, and =CD_2 groups was identified (except *III* and *IV*) with the aid of its doublet due to crystal field perturbations[1], the =C— (H, D) stretching frequencies were also easily located. Having not carried out a normal coordinate analysis of the complexes d_0, *I — VII* we did not try to assign all the bands relevant to the coordination bond.

DISCUSSION

It should be stressed again that the interpretations mentioned in the Introduction had been based on comparison of IR spectra of coordinated alkenes to the spectra of the free alkenes, *i.e.* to those of the free molecules in the ground electronic state. However, Mason and coworkers[24,25] have pointed out that the Dewar's[26] and Chatt–Duncanson's[7] models for some metals and coordinated alkenes implicate that "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 ... 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 ... state"[25]. Hence, any interpretation of the IR spectrum of a coordinated alkene should also involve a comparison with spectra of the free, however electronically excited molecules of that alkene (*cf.* also[22]).

The vibrational spectra of free, electronically excited molecules are not yet known due to their short life-times. Some "vibrational information" is accessible in the high resolution electronic spectra of gases which is, however, limited to vibrations of bonds from which an electron was excited either by absorption of a photon (UV absorption spectra, photoelectron spectra UPES) or by a collision energy transfer (Penning ionization electron spectra, electron impact spectra). The species resulting from such

experiments generally are: a neutral electronically excited molecule (UV absorption), a radical-cation (UPES, Penning ionization, electron impact) or a radical-anion (electron impact).

In the case of propene coordinated in ZS, there are three extreme cases of bonding according to Chatt-Duncanson model[7]: *1)* only σ-bonding (forward-donation of electron from propene to Pt) is involved so that a radical-cation-like species of propene is formed, *2)* both σ- and π-bonding (back-donation of electron from Pt to propene π^*-antibonding orbital) are involved so that a neutral excited-like ($\pi \rightarrow \pi^*$ or N $\rightarrow$ V transition) species of propene is formed, and *3)* only π-bonding is acting, leading to a radical-anion-like species of propene. This case is very improbable.

A comparison of the free, excited species of propene to propene coordinated in ZS is made in Fig. 2. Here are presented the two vibrations associated with the original C=C bond from which one π-bonding electron was excited according to Franck-Condon's principle. These are the (C=C)* stretching and the (C=C)* torsion or =CH$_2$ twisting vibrations.

Now, it is necessary to clear one terminological problem connected with the C=C torsion or =CH$_2$ twisting vibration, potential barier of which governs *cis-trans* isomerizations in alkenes with an internal C=C bond[27]. "Chemical spectroscopists" tend to call it exclusively the =CH$_2$ twisting mode (or, generally, =C—H out-of-plane deformation) without considering that $(2p_x)_\pi$ orbital overlap is simultaneously twisted during this vibration. If one π-electron is removed from the C=C bond either by photoexcitation or by coordination bond formed, the bond order of the carbon–carbon linkage decreases from 2 to 1·5 (*cf.* ethylene in ZS[28]) and the bond becomes vibronically excited. For this reason, the fundamental frequency and overtones of the (C=C)* torsion are greatly reduced (in ethylene the first overtone has been found at about 400 cm^{-1})[27]. As a consequence, the term "twisting =CH$_2$" has prevented searching this vibration in the region below 600 cm^{-1} of the spectra of coordinated alkenes, although the corresponding band has been recorded[8].

In this connection, another problem related to the C=C stretching vibration is its vibrational coupling with the =CH$_2$ scissoring mode in free molecules and "a vibrational decoupling" after deuteration and coordination. The calculated potential energy distribution for free propenes-d_x proved[21] that a contribution of the scissoring mode to the C=C stretching changes from 13% (d_0) to 15% (2-d_1) and to less than 10% in CH$_3$. HC=CD$_2$. It is in accordance with Fig. 1, where "the decoupling" is assumed in all the cases of 1-deuterium substitution (*II – VII*). This is the cause of upward ν(C=C)* shifts compared to the cases d_0 and *I* where the coupling after coordination was not loosen so extensively.

Summarizing, we propose that in 1-decene-d_x analogs of ZS ($d_0, I - VII$) the alkene is bound to Pt as a near-radical-cation species after analogy with the coordinated propene. The evidences are the two vibrational bands near 1400 and 550 cm^{-1}. This means that the sp^2-hybridization of the two carbon atoms is retained but not

the $C=C$ bond order $(2 \rightarrow 1.5)$. The electronic part of the "bond excitation" is realized through the coordination bond between 1-decene and Pt-atom and this "electronic excitation" of the ligand and Pt is preserved as long as the complex exists. The near-radical-cation state means that nearly one π-electron was removed from the $C=C$ bond of 1-decene, however a new, three-centre molecular orbital was formed and not an ion pair. One IR band near 400 cm^{-1} corresponds to one σ-coordination bond (point group of symmetry of $[\text{PtCl}_3(1\text{-decene})]$ is C_1). From this point of view we do not deny the concept[7,26] of an electron back-donation from Pt to alkene, however, we believe that back-bonding from Pt to alkene is not identical with the formation of the two Pt — C bonds.

This picture of bonding implies that a revision of the interpretation[1] of the vibrational spectra of ZS is needed because one of the bands (404, 492 cm^{-1}) presumably belongs to the vibronically excited $(C=C)^*$ torsion and not to the second PtC$_2$ bond. This will be the subject of a subsequent publication[29]. As a concluding remark we note that vibrational spectra of some alkene coordination complexes could offer a tool for studies of excited-like species with very long life-times. They represent vibrational-electronic (vibronic) problems of complexes the fragments of which are virtually identical with their excited states. Moreover, full "vibrational information" is measurable, giving also some account of electronic excitation. These data could be useful for interpretations of vibrational structures in electronic spectra of free alkenes which, in turn, can enable the proper assignment of vibrational spectra of coordinated molecules. The two approaches clearly complement each other.

REFERENCES

1. Hiraishi J.: Spectrochim. Acta *A 25*, 749 (1969).
2. Babushkin A. A., Gribov L. A.: Dokl. Akad. Nauk SSSR *123*, 461 (1958).
3. Ware M. J.: Unpublished results.
4. Woodward L. A.: Pure Appl. Chem. *11*, 473 (1965).
5. Hubert J., Kong P. C., Rochon F. D., Theophanides T.: Can. J. Chem. *50*, 1596 (1972).
6. Powell D. B., Scott J. G. V., Sheppard N.: Spectrochim. Acta *A 28*, 327 (1972).
7. Chatt J., Duncanson L. A.: J. Chem. Soc. *1953*, 2939.
8. Grogan M. J., Nakamoto K.: J. Am. Chem. Soc. *90*, 918 (1968).
9. Adams D. M.: *Metal-Ligand and Related Vibrations*, p. 186. Arnold, London 1967.
10. Fritz H. P., Sellmann D.: J. Organometal. Chem. *6*, 558 (1966).

11. *Documentation on Molecular Spectroscopy, IR Spectrum No* 2796. Butterworths, London.
12. Pánková M., Vítek A., Vašíčková S., Řeřicha R., Závada J.: This Journal *37*, 3456 (1972).
13. Řeřicha R., Vítek A., Vašíčková S., Pánková M., Závada J.: This Journal *37*, 3749 (1972).
14. API Research Project 44: *Catalog of Infrared Spectral Data. Spectra Nos* 3087—3093.
15. Chatt J., Searle M. L.: Inorg. Synt. *5*, 210 (1957).
16. Anderson J. S.: J. Chem. Soc. *1936*, 1042.
17. Vítek A.: Unpublished results.
18. Babushkin A. A., Gribov L. A., Gelman A. D.: Ž. Neorgan. Chim. *4*, 1542 (1959).
19. Adams D. M., Chatt J.: J. Chem. Soc. *1962*, 2821.
20. Sverdlov L. M., Kovner M. A., Krainov E. P.: *Vibrational Spectra of Polyatomic Molecules*, Chap. 5. Wiley, London 1973.
21. Silvi B., Labarbe P., Perchard J. P.: Spectrochim. Acta *A 29*, 263 (1973).
22. Brundle C. R., Brown D. B.: Spectrochim. Acta *A 27*, 2491 (1971).
23. Samson J. A. R., Marmo F. F., Watanabe K.: J. Chem. Phys. *36*, 783 (1962).
24. Mason R.: Nature *217*, 543 (1968).
25. McWeeny R., Mason R., Towl A. D. C.: Discussions Faraday Soc. *47*, 20, 59 (1969).
26. Dewar M. J. S.: Bull. Soc. Chim. France *18*, C 79 (1951).
27. Merrer A. G., Mulliken R. J.: Chem. Rev. *69*, 639 (1969).
28. Kató H.: Bull. Chem. Soc. Japan *44*, 348 (1971).
29. Řeřicha R.: Unpublished results.
30. Jones R. N., Sandorfy C. in the book: *Technique of Organic Chemistry*, Vol. IX (W. West, Ed.), 1st Ed., p. 347. Interscience, New York 1956.
31. Farina M., Peraldo M.: Gazz. Chim. Ital. *90*, 973 (1960).
32. El-Sabban M. Z., Zwolinski B. J.: J. Mol. Spectry. *27*, 1 (1968).
33. Katrib A., Rabalais J. W.: J. Phys. Chem. *77*, 2358 (1973).
34. Čermák V., Ozenne J. B.: Int. J. Mass Spectr. Ion Phys. *7*, 399 (1971).

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