Recent developments of FT-IR and Raman spectroscopy in coordination chemistry

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Abstract - The nature of the bond between a metal and an unsaturated hydrocarbon is one of the most fundamental and significant problems in coordination chemistry. In spite of wide structural and spectroscopic studies of olephinic π-complexes a number of fundamental spectroscopic properties have not been clearified yet. Reinvestigation of FT-IR and Raman spectra of $K[Pt(C_2H_4)Cl_3]$ and $K[Pt(C_2H_4)Cl_3].H_2O$ in both the solid phase and water/HCl solution suggests some modification of widely accepted assignments. Skeletal modes of $[NBu_4][Pt(C_2H_4)Br_3]$, $[NBu_4][Pd(C_2H_4)Cl_3]$ and their C_2D_4 derivatives have been measured and assigned. A new model for the normal coordinate treatment of π-complexes has been adopted to calculate metal-ligand force constants.

INTRODUCTION

The impressive development that the coordination chemistry of transition metals experienced in the last 25 years has led to a dramatic change in conceptions of chemical bond. The new field of transition metal chemistry now becomes one of the most important and exciting areas of chemical research. It acquires a more and more significant role in several fields e.g. catalysis, biochemistry and protection of environment, investigations connected with semiconductors or new sources of energy etc. Among the rapidly increasing chemical, physical and biological investigations the number of molecular structure studies is also growing year by year. The investigation of coordination compounds has focused fundamentally on the chemical bond between the metal and its environment that is the ligand.

Vibrational (infrared and Raman) spectroscopy has played and is playing a very important role, as it is one of the most efficient methods of molecular structure studies with the help of which direct information can be obtained about the nature of metal-ligand bonds in many cases.

For studying the metal-ligand vibrations far-infrared and Raman spectroscopic equipment is required. In the last 10-15 years there has been a considerable development especially in the FT-IR measurement techniqe; this and also the very recent appearance of FT-Raman spectroscopy offer better and better instrumental background for structural studies of coordination compounds.

A great number of papers have been published annually on the subject of IR and Raman spectroscopy of coordination compounds. A comprehensive treatment of the vibrational spectra of coordination compounds to give a complete general survey of the reported literature is practically impossible in the frame of a short paper. Therefore the present paper is dealing with some selected IR, FIR and Raman spectra of transition metal-ethylene complexes, studied recently in our laboratory.

In spite of a considerable amount of earlier work on Zeise's salt, $K[Pt(C_2H_4)Cl_3].H_2O$, there are still some open questions regarding the vibrational assignment of the spectra (see ref. 2 and references therein). The basic work of Hiraishi (ref.2) led to a generally accepted assignment (ref.3).

Most of the recently used vibrational assignment (refs. 3-4) were based on relatively early experimental studies (refs.2, 6-7) and the only publication of Hiraishi (ref. 2) dealing with polarization studies of the Raman spectra

in solution. There have been conflicting reports concerning the vibrational assignments of the spectra of Zeise's salt, largely due to the complexity of the spectra.

A recent inelastic neutron scattering study by Jobic (ref.8) suggested important experimental improvement for the very rarely studied vibrations of a_2 and b_2 species. In our recent study (ref.9) the skeletal modes of $[Pt(C_2H_4)_3]$, $[NBu_4][Pt(C_2H_4)Cl_3]$ and $[NBu_4][Pt(C_2D_4)Cl_3]$ have been assigned. However no detailed far-infrared and Raman spectroscopic studies have been performed to date for PtBr and and PdCl analogues. In this paper we are going to describe a reinvestigation of Zeise's salt, and in addition, discuss some results obtained from the spectra of $[NBu_4][Pt(C_2H_4)Br_3]$ and $[NBu_4][Pd(C_2H_4)Cl_3]$, including their C_2D_4 derivatives.

EXPERIMENTAL

The infrared spectra were recorded using a DIGILAB FTS-20C FT-IR system. Far-infrared measurements were performed using a Nicolet 7999A and a DIGILAB FTS-14C systems. The Raman spectra were recorded with a Jobin-Yvon Ramanor HG-25 holographic grating double monochromator spectrometer using the excitation from Carl Zeiss (DDR) He-Ne, argon- and kripton-ion lasers. The preparation of Zeise's salt analogues will be desribed elsewhere (ref.10).

REINVESTIGATION OF ZEISE'S SALT

In our earlier investigation (ref.11) of $Pt(C_2H_4)_3$ three polarized Raman lines at 1617, 1338 and 1226 cm^{-1} were reasonably assigned to CC stretching, CH_2 scissoring and CH_2 wagging vibrations, respectively. Hiraishi (ref.2) observed only one polarized band for Zeise's anion in this region, at 1241 cm^{-1}, which he assigned to CC stretching strongly coupled with the CH_2 scissoring motion at 1522 cm^{-1}; the band at 975 cm^{-1} was assigned to CH_2 wagging mode. Since we were not able to record the latter band neither in IR nor in Raman spectra, and we observed the wagging mode for tris(ethylene)platinum above 1200 cm^{-1}, it appeared to be necessary to revise the vibrational assignment of Zeise's anion.

The selected fundamental bands for the IR, FIR and Raman spectra of the anhydrous (A), hydrated (B) and tetrabutylammonium (D) derivative of Zeise's salt are reported in Table 1. It is interesting to note that a number of anion frequencies are slighthly different for these three complexes.

The Raman active CH stretching mode and the polarized band were assigned to a_2 and a_1 species, respectively. Two sets of frequencies, 1517, 1241, 1023 and 1517, 1410, 1241 cm^{-1} can be assigned to the strongly coupled CC stretching, CH_2 scissoring, and CH_2 wagging modes, respectively. The second set shows better agreement with tris(ethylene)platinum spectrum, so this assignment is figurating in Table 1. At this stage we are not able to decide which assignment is more realistic. Other ethene deformation bands of a_2 and b_2 species were assigned on the basis of INS experiment (ref.8). Since the low frequency part of the vibrational spectra of Zeise's anion $K[Pt(C_2H_4)Cl_3].H_2O$ is obscured by librational modes of water (see e.g. the 508, 407, 160 and 93 cm^{-1} bands), and FIR data in solution of the salt are unknown, we prepared the corresponding salts with the composition: $[NBu_4][Pt(C_2H_4)X_3]$ and $[NBu_4][Pt(C_2D_4)X_3]$ (X=Cl, Br). The tetrabutylammonium salts are soluble in most of the organic solvents used for spectroscopy and therefore solution Raman (with polarizability measurements) and IR, FIR measurements become possible. We were able to detect most of the important low frequency fundamental vibrational bands of Zeise's anion and consequently the assignment of the 550-180 cm^{-1} range of the vibrational spectra is relatively problemless. In the low frequency range all polarized lines were assigned to a_1 species and the other motions can be identified by comparison with the C_2D_4 analogue and the $[PtCl_3(CO)]^-$ anion (ref.13).

In spite of the fact that Zeise's salt has been studied by a great number of famous spectroscopists, there are a number of points in the assignment which need further experimental and theoretical work for achieving deeper understanding the ethylene ligand vibrations.

TABLE 1. Fundamental frequencies of Zeise's $[Pt(C_2H_4)Cl_3]^-$ anion (cm^{-1})

A solid	B solid	C solution	D solution	Assignments	
3095 m	3094 s		3093 s	b_2	
3074 s	3074 vs		3075 vw	a_2	CH stretching
3007 m	3042 m	3020 vw	3042 w	a_1	
2965 m	2984 m,s	2990 w	3011 s	b_1	
1528 w	1522 w	1523 w(0.65)	1517 w,b,p	a_1	CC stretching
1422 vs	1426 s	1426 vw,dp	1424 s	b_1	CH$_2$ scissoring*
1415 s	1419 vs	1410 vvw?	1415 sh	a_1	
1253 vvs	1240 vs	1241 vs(0.22)	1234 vs,p	a_1	CH$_2$ wagging*
1189 vw	1179 vw			a_2	CH$_2$ rocking
1024 vs	1032 s	1023 vw(0.65)	1009 s	b_1	CH$_2$ wagging*
846 vw	841 vw		824 vw	b_2	CH$_2$ rocking
736 w	734 w	728 vw,dp	732 w	b_2	CH$_2$ twisting
492 m	488 m	490 s(0.64)	501 w	b_1	PtC$_2$ tilt(asym.str.)
398 s	397 s	400 s(0.27)	410 s,p	a_1	PtC$_2$ sym.stretching
338 vs	335 vs	336 vs(0.29)	338 vs,p	a_1	PtCl$_2$ sym.stretching
334 s	328 sh	330 sh	332 sh,p	a_1	PtCl stretching
312 vw	306 s	308 m,dp	316 m,dp	b_2	PtCl$_2$ asym.stretching
215 s	210 m	210 w,dp	214 w,dp	b_1	PtC$_2$ (rocking)
184 s	178 m	167 w,dp	170 w	b_1 b_2	PtCl$_2$ o.o.p. bend. PtCl$_2$ i.p. bend.
123 w	124 m		147 w,p	a_1	PtCl$_2$ i.p. bend.
			108 w,b	b_2	ClPtC$_2$ i.p.bend.

A: $K[Pt(C_2H_4)Cl_3]$; B:$K[Pt(C_2H_4)Cl_3].H_2O$; C: Raman spectrum of Zeise's salt in H$_2$O-HCl solution (depolarization ratios are given in brackets); D:$[NBu_4][Pt(C_2H_4)Cl_3]$ in CDCl$_3$
Remarks: The bands underlined in columns A,B and D are from the Raman spectra; *Band assignments, see text.

TABLE 2. Skeletal vibrational bands (cm^{-1}) of $[NBu_4][Pt(C_2H_4)Br_3]$ and $[NBu_4][Pt(C_2D_4)Br_3]$

$[Pt(C_2H_4)Br_3]^-$		$[Pt(C_2D_4)Br_3]^-$		Assignment	
IR*	Raman*	IR*	Raman*		
1510 w	1514 w	1333 s	1336 w	a_1	C=C stretching
492 w	505 w	454 w	465 w	b_1	PtC$_2$ tilt(asym.str.)
399 m	407 m	383 m	397 m	a_1	PtC$_2$ sym.str.
241 vs	–	239 vs	–	b_2	PtBr$_2$ asym.str.
220 s	223 s	219 s	224 s	a_1	PtBr stretch.
201 s	204 vs	201 w	204 vs	a_1	PtBr$_2$ sym.str.
(201 s)	(204 vs)	187 s	188 w	b_1	PtC$_2$ rocking
114 vw	117 sh	116 s	118 sh	b_2	PtBr$_2$ i.p.bend.
–	108 m	–	108 m	a_1	PtBr$_2$ i.p.bend.
84 w	–	–	70 vw,b	b_2	BrPtC$_2$ i.p.bend.

*IR spectra of CH$_2$Cl$_2$ solutions and Raman spectra of solids

VIBRATIONAL SPECTRA OF OTHER ZEISE'S SALT ANALOGUES

The only bromo analogue of the anhydrous Zeise's salt has been studied by IR spectroscopy (ref.7). Here we report the skeletal modes of $[NBu_4][Pt(C_2H_4)Br_3]$ and its deutero-ethylene analogue. (Table 2). Assignments are partly based on Table 1 and on those for the $[PtBr_3(CO)]^-$ anion (ref.13). The PtC_2 tilting and rocking modes were identified by comparison with C_2D_4 analogue. The latter band is totally overlapping with the $PtBr_2$ symmetric stretching mode around 200 cm^{-1} in the light isotope. The PtC_2 rocking mode shifted down from the position of the $PtBr_2$ stretching band was observed at 187 cm^{-1} for $[Pt(C_2D_4)Br_3]^-$ analogue. It is interesting to note that all vibrations assigned to the PtC_2 group are lowered by about 10 cm^{-1} for bromide analogue as compared to those of the $[NBu_4][Pt(C_2H_4)Br_3]$ molecule.

The $[NBu_4][Pd(C_2H_4)Cl_3]$ and its C_2D_4 analogue were prepared _in situ_ in different organic solvents and the spectra were measured in solution. Three PdCl stretching bands measured in FIR spectrum of $[Pd(C_2H_4)Cl_3]^-$ anion have been reported (ref.14). The skeletal IR bands of palladium Zeise's salt analogues are presented in Table 3. Unfortunately the CC stretching and PdC_2 symmetric stretching modes were definitely observed only in the deuterated sample and the 1560 and 370 cm^{-1} frequencies were estimated from 1380 and 345 cm^{-1} bands of $[Pd(C_2D_4)Cl_3]^-$, respectively. The skeletal deformation modes were assigned on the basis of $[PdCl_3(CO)]^-$ anion (ref.13). According to the isotope effect of the C_2D_4 ligand, the PtC_2 tilting, symmetric stretching and rocking modes can be easily assigned. We would like to emphasize the strong metal sensitivity of the MC_2 symmetric stretching and especially the MC_2 tilting vibrations. These modes were observed at 390 and 460 cm^{-1} for $[Pt(C_2D_4)Cl_3]^-$ (ref.8) which are shifted to 345 and 387 cm^{-1} in the case of $[Pd(C_2D_4)Cl_3]^-$.

TABLE 3. Skeletal IR bands for $[Pd(C_2H_4)Cl_3]$ and $[Pd(C_2D_4)Cl_3]$ anions (cm^{-1})

$[Pd(C_2H_4)Cl_3]^-$	$[Pd(C_2D_4)Br_3]^-$		Assignment
(1560)	1380 m	a_1	CC stretch
428 vw	387 w	b_1	PdC_2 tilt (asym.str.)
(370)	345 sh	a_1	PdC_2 sym.str.
338 vvs	333 vvs	b_2	$PdCl_2$ asym.str.
318 m	316 w,m	b_1	$PdCl_2$ asym. str.
292 m	288 w,m	a_1	$PdCl_2$ (trans) str.
207 w	194 w	b_1	PdC_2 rocking
178 vw	178 vvw	b_2	$PdCl_2$ i.p.bend.
155 sh	155 sh	b_1	$PdCl_2$ o.o.p.bend.
149 w	147 w	a_1	$PdCl_2$ i.p. bend

Remarks: In brackets estimated frequencies.
          FIR spectra were measured in solution of $CDCl_3$ with
          10% CH_2Cl_2

DISCUSSION

A comparison of the metal-ligand stretching frequencies is shown in Table 4. The PtCl stretching frequencies were in an average 11% higher for the CO complex and 8% higher for the PdCl stretching bands. The good π-acceptor and weak σ-donor nature of CO will result in a greater positive charge on the metal than that for ethylene and this will increase PtCl and PdCl bond strengths. It is interesting to note that this effect is not clearly observable for bromide-platinum bonding of CO and C_2H_4 complexes.

A new and simple normal-coordinate treatment using rigid body approximation for π-complexes has been suggested (ref.12). The metal-ethylene skeletal force constants were calculated for ethylene complexes listed in Table 5. The CC stretching force constants were determined by using an "effective" G matrix element, determined from the normal coordinate analysis of the

TABLE 4. Comparison of metal-ligand stretching frequencies between
$[MCl_3(CO)]^-$ and $[M(C_2H_4)Cl_3]^-$ (M=Pt(II), Pd(II)) (cm^{-1})

$[PtCl_3(CO)]^-$	$[Pt(C_2H_4)Cl_3]^-$	$[PdCl_3(CO)]^-$	$[Pd(C_2H_4)Cl_3]^-$	Assignment	
497	410	416	(370)	a_1	$\nu(MC)$
345	338	331	318		$\nu_s(MCl_2)$
344	332	350	338		$\nu(MCl)$
540	501	475	428	b_1	tilt*
322	316	300	292	(b_2)	$\nu_a(MCl_2)$**

Remarks: *For CO complexes tilt mode refers to MCO o.o.p. linear bendings;
**for ethylene complexes MCl_2 asym. stretching mode falls in b_2 symmetry
species.

complete $[Pt(C_2H_4)Cl_3]^-$ anion (ref.15). ($K(CC)=\lambda/G_{eff}$ where G_{eff}=0.18373
for C_2H_4 and 0.15443 for C_2D_4 ligands, respectively, and λ is the eigenvalue
of the CC stretching frequency). As appears from our studies of ethylene
complexes that metal-ligand stretching force constants for Pt is
significantly larger than those for Pd. Between Pt and Pd $K_1(MC_2)$ decreases
by 28% while the CC stretching force constant increases by 6% only. The much
greater response of $K_1(MC_2)$ than K(CC) implies that the change in π-bonding
is only a part of the effect on MC bond. The behaviour of the CC stretching
force constant demonstrates the greater degree of π-donation from the metal
in the case of platinum but the much greater relative change in the M-C force
constant must be the result of both, the increased σ-covalency and the
increased degree of π-bonding in the Pt-C bond. Since the bond lengths in the
ethylene complex of the two metals should be very similar, the difference
must largely be due to better overlapp of the 5d orbital that 4d in its
contribution the σ-bonding resulting in increases covalency. Very similar
behaviour can be established on the basis of $H_1(MC_2)$, tilting force
constants.

The higher CC stretching and lower PtC_2 stretching force constants for
$[Pt(C_2H_4)_3]$ and $[Pd(C_2H_4)Cl_3]^-$ as compared to the Zeise's salt analogues are
in agreement with their much lower stability and so they have much weaker
metal-ethylene bond.

TABLE 5. Selected skeletal force constants of etylene complexes

Compound	K(CC) (str.)	$K_1(MC_2)$ (str.)	$H_1(MC_2)$ (tilt)	$K_2(MC_2)$ (rock.)	Remarks
$[NBu_4][Pt(C_2H_4)Cl_3]$	7.17(18)	2.44(2)	2.50(16)	0.65(1)	a
$K[Pt(C_2H_4)Cl_3]$	7.31(18)	2.34(5)	2.23(*)	0.67(*)	
$K[Pt(C_2H_4)Cl_3].H_2O$	7.24(19)	2.34(5)	2.34(10)	0.67(2)	
$[NBu_4][Pt(C_2H_4)Br_3]$	7.07(27)	2.34(4)	2.56(18)	0.58(1)	a
$[NBu_4][Pd(C_2H_4)Cl_3]$	7.54(27)	1.75(2)	1.74(5)	0.55(1)	
$[Pt(C_2H_4)_3]$	7.99(20)	1.66(6)	2.04**	0.65(3)	b

Units: $K=10^2 Nm^{-1}$, $H=10^{-18}$ Nm rad^{-2}
(*) No spectrum of deuterated sample, the calculated
frequencies are 431 and 203 cm^{-1} for tilt and rock modes,
respectively.
a - From ref. 12; b - From ref. 9.
**Calculated from e' species, the a_2" tilt mode is inactive.

The $K_1(MC_2)$ stretching force constant, calculated by the rigid body approximation can be transformed to one metal-carbon bond direction of metallocyclopropane model. For example, the resulting k(PtC)=1.29 Ncm^{-1} for Zeise's salt is in a reasonable agreement with Hiraishi's 1.45 Ncm^{-1} (ref.2), with Jobic's 1.36 Ncm^{-1} (ref.8) and with our 1.34 Ncm^{-1} (ref.15) values originating from a complete solution of the vibrational problem. It is also clear that the point mass model should give a K_1 value practically identical whith the result of the rigid body approximation; this is the reason that K_1=2.23 Ncm^{-1} in ref.6 is in agreement with the figures of potassium salts in Table 5.

Finally we would like to emphasize that the rigid body approximation model suggested by us for π-complexes is a simple but very useful one for fast understanding the vibrational properties connected with metal-ethylene motions.

Acknowledgements

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