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Spectroscopic and theoretical study of $[PdCl_3(C_2H_4)]^-$ and $[PdCl_3(C_2D_4)]^-$ complexes

É. Bencze [a], I. Pápai [a], J. Mink [a,b,*], P.L. Goggin [c]

[a] *Institute of Isotope and Surface Chemistry, Chemical Research Center, Hungarian Academy of Sciences, PO Box 77, H-1525 Budapest, Hungary*
[b] *Department of Analytical Chemistry, University of Veszprém, PO Box 158, H-8201 Veszprém, Hungary*
[c] *Inorganic Chemistry Department, Bristol University, Bristol BS8 1TS, UK*

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Abstract

FTIR and FT-Raman spectra of $[PdCl_3(C_2H_4)]^-$ and $[PdCl_3(C_2D_4)]^-$ anions have been recorded at greater sensitivity than hitherto and assigned on the basis of the well-studied Zeise's salt. Density functional theory (DFT) calculations were performed in order to obtain the optimised geometry, the vibrational frequencies and IR intensities of the Pd-complex. The comparison of the theoretical infrared spectra, the H/D isotopic shifts and the shifts in the CC stretching and CH scissoring frequencies upon coordination with those from experimental study show a remarkable agreement for the $[PdCl_3(C_2H_4)]^-$ and $[PdCl_3(C_2D_4)]^-$ species. The optimised PdC bond distance is 2.197 Å, indicating that the metal–ligand bond is weaker in $[PdCl_3(C_2H_4)]^-$ than in Zeise's salt but C_2H_4 seems to be more distorted in the Pd-analogue. The calculated force constants also confirm the lower stability of the Pd-complex. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Palladium; FTIR; FT-Raman spectroscopy; Normal coordinate analysis; Density functional theory

1. Introduction

The study of bonding between a metal and an unsaturated hydrocarbon plays a significant role in organometallic chemistry. Transition metal–ethylene complexes provide a primary model for the analysis of bonding in π-complexes. Vibrational (infrared and Raman) spectroscopy is one of the most efficient methods of molecular structure studies. Moreover, theoretical calculations, as a complementary tool, provide a deeper understanding of the spectra and complex structures.

Zeise's salt is one of the most widely investigated ethylene π-complexes (e.g. [1–5]). By contrast the Pd-analogue has not been studied in detail; this is because salts containing the $[PdCl_3(C_2H_4)]^-$ anion cannot be isolated as solids although they can be readily formed from $[Pd_2Cl_6]^{2-}$ salts, which are soluble in solvents such as CH_2Cl_2 in which C_2H_4 is also easily soluble according to the equilibrium

$$[Pd_2Cl_6]^{2-} + 2C_2H_4 \leftrightarrows 2[PdCl_3(C_2H_4)]^-$$

which under such circumstances has overwhelmingly moved to the right-hand side.

Far-IR spectra of $[Cl_3(C_2H_4)]^-$ [6] and skeletal IR modes of light and deuterated species have been published [5].

In this study we intend to reinvestigate the vibrational assignment of the spectra of the Pd-analogue–Zeise's salt based on new FT-Raman measurements, density functional theory (DFT) calculations of vibrational frequencies and IR intensities. Full normal coordinate analysis (NCA) has been performed based on the model described in ref. [7], introducing nonredundant internal co-ordinates.

2. Experimental

The Pd–Zeise's salt $[NBu_4][Pd(C_2H_4)Cl_3]$ and its C_2D_4-analogue were prepared [6] in situ in different organic solvents and the infrared spectra were measured on a 10% CH_2Cl_2 + 90% $CDCl_3$ solution.

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* Corresponding author. Tel.: +36-1-395-9285; fax: +36-1-395-9285.

E-mail address: mink@iserv.iki.kfki.hu (J. Mink)

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Table 1
Experimental and calculated equilibrium geometrical parameters for various ethylene complexes (distances in Å, angles in °)

	$Pd(C_2H_4)$	$[PdCl_3(C_2H_4)]^-$	$[PtCl_3(C_2H_4)]^-$
	Calc. [a]	Calc.	Exp. [b]
r(MC)	2.053	2.197	2.132
r(CC)	1.414	1.395	1.375
r(CH)	1.109	1.103	1.087
$r(MCl_t)$	–	2.372	2.340
r(MCl)	–	2.398	2.302
α(HCH)	115.1	118	115
$\alpha(ClPdCl_t)$	–	91	90.24
Tilt [c]	20.8	16.96	16.25

[a] Ref. [15].

[b] Ref. [16].

[c] Tilt is the angle between the bisector of the HCH bond angle and the C–C bond.

FTIR and FTFIR measurements were done using a Bio-Rad Digilab FTS-60A system and a Bio-Rad Digilab Division FTS-40 spectrometer, respectively. Raman spectra were measured with a BIO-RAD Digilab dedicated FT-Raman spectrometer using the excitation from Nd:YAG laser. FT-Raman investigations were carried out on dried CH_2Cl_2 solution.

3. Computational details

The NCA calculations were performed using a program reported previously [8], which has been updated [9] for IBM-PC-compatible computers.

The density functional calculations were carried out with the Gaussian 94 package [10]. The geometry optimisation and the calculation of the harmonic frequencies and infrared intensities were obtained at the gradient-corrected level of theory using the BP86 functional [11,12]. All electron orbital basis sets were employed for all atoms, which had the following contraction patterns: (633321/53211/531) for Pd [13], (6321/521/1) for Cl [13], (5211/411/1) for C [14], and (41/1) for H [14].

4. Results and discussion

The calculated geometrical parameters for different ethylene complexes are compared to experimental values for the Zeise's salt in Table 1. By comparison of the calculated geometrical data in the case of the two Pd complexes, $Pd(C_2H_4)$ and $[PdCl_3(C_2H_4)]^-$, we can conclude that these data are in line with their stability order. The longer PdC bond and the shorter CC bond in the case of $[PdCl_3(C_2H_4)]^-$ indicate a weaker Pd–ethylene bond as compared to $Pd(C_2H_4)$. Table 1 also shows that the metal–ligand bond is stronger in $[PtCl_3(C_2H_4)]^-$ than in the Pd analogues, by inference from the MC distances, but the CC bond appears to be shorter rather than longer as might have been expected. The C_2H_4 moiety does appear to be slightly more distorted from planarity in $[PdCl_3(C_2H_4)]^-$ than in the platinum salt. In Ref. [17] the calculated geometrical parameters for $[PdCl_3(C_2H_4)]^-$ (r(PdC) = 2.350 Å, r(CC) = 1.354 Å) indicate less distortion of C_2H_4 during the complexation. The higher value obtained for the

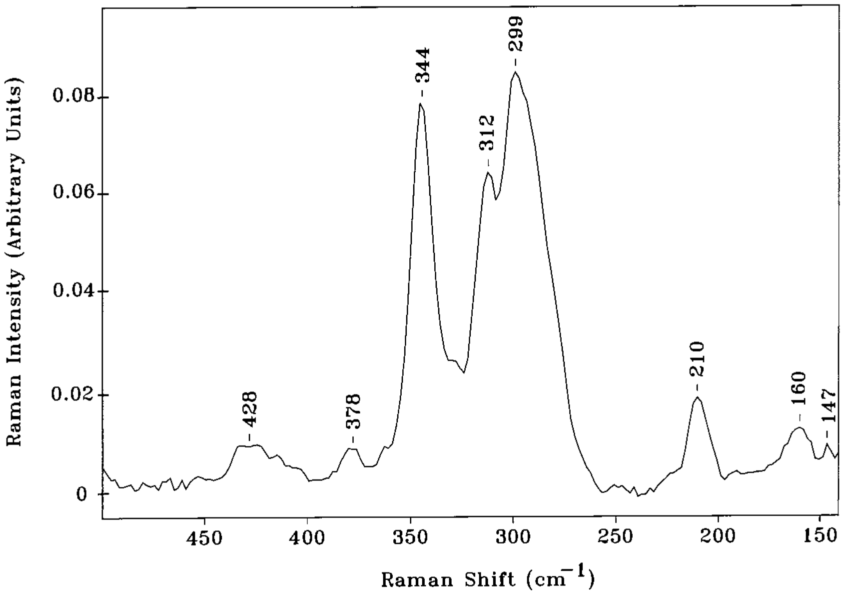

Fig. 1. The low-frequency region of the FT-Raman spectrum of $[PdCl_3(C_2H_4)]^-$ anion after solvent bands subtraction, recorded at 510 mW laser power and 4096 scans.

Table 2
Calculated and experimental fundamental frequencies (cm^{-1}) for palladium–ethylene complexes [a]

	Pd(C$_2$H$_4$)		[PdCl$_3$(C$_2$H$_4$)]$^-$			[PdCl$_3$(C$_2$D$_4$)]$^-$		Assignment
	Calc. [15]	Exp. [18]	Calc.	Exp.		Calc.	Exp.	
				IR [5]	Raman		IR [5]	
a_1	3010	2952	3044 (6)	–	2876 m	2232	–	CH str.
	1473	1502	1495 (3)	–	1526 w	1364 (4)	1380 m	C=C str. + CH$_2$ sciss.
	1204	1223	1241 (2)	–	1267 m	929	–	CH$_2$ sciss. + C=C str.
	902	913	913 (15)	–	1086 vs	681	–	CH$_2$ wag.
	481	–	351 (3)	[370]	378 vw	341 (4)	345 sh	PdC$_2$ str.
	–	–	288 (27)	318 m	312 m	284 (25)	288 wm	PdCl$_2$ str.
	–	–	248 (6)	292 wm	299 vs	247 (7)	316 wm	PdCl$_t$ str.
	–	–	144 (0.2)	149 vvw	147 vvw?	143 (0.2)	147 w	PdCl$_2$ i.p. bend.
a_2	3058	–	3133 (0)	–	2937 w *	2337	–	CH str.
	760	–	1181 (0)	–	–	952	–	CH$_2$ rock.
	570	–	923 (0)	–	–	657	–	CH$_2$ twist.
	–	–	148 (0)	–	147 vvw *?	124	–	C$_2$ torsion
b_1	3006	–	3042 (7)	–	2876 m	2197	–	CH$_2$ str.
	1374	–	1376 (9)	–	1338 w	1021	–	CH$_2$ sciss.
	923	–	902 (5)	–	907 m	727	–	CH$_2$ wag.
	433	–	405 (0.3)	428 vw	428 vw	365 (0.2)	387 w	PdC$_2$ tilt
	–	–	126 (3)	155 sh	160 w	124 (3)	155 sh	PdCl$_2$ o.o.p. bend.
	–	–	66 (2)	–	–	63	–	PdC$_2$ rock.
b_2	3088	–	3152 (1)	–	2937 w	2349	–	CH$_2$ str.
	1150	–	792 (1)	–	–	570	–	CH$_2$ rock.
	869	–	579 (0.2)	–	–	425	–	CH$_2$ twist.
	–	–	297 (71)	338 vvs	344 vs	294 (70)	333 vvs	PdCl$_2$ str.
	–	–	187 (3)	207 w	210 wm	174 (2)	194 w	PdC$_2$ wag.
	–	–	137 (1)	178 vw	–	137 (1)	178 vvw	PdCl$_2$ i.p. bend.

[a] In parentheses, calculated IR intensities. In square brackets, estimated frequency.
* Frequencies used twice.

Table 3
Some stretching force constants (10^2 N m^{-1}) of Zeise's salt analogues

Compound	K(C=C)	K(MC)	F(MC,MC)	K(MX)	F(MX,MX)	K(MX$_t$)
[Pt(C$_2$H$_4$)Cl$_3$]$^-$	7.60	1.67	−0.37	1.86	0.503	2.02
[Pt(C$_2$H$_4$)Br$_3$]$^-$	7.39	1.70	−0.37	1.84	0.203	1.72
[Pd(C$_2$H$_4$)Cl$_3$]$^-$	7.93	1.19	−0.31	1.72	0.366	1.88

PdC bond is probably due to the fact that the electron correlation has not been considered in the calculations.

The low-frequency region of the solution Raman spectrum of [PdCl$_3$(C$_2$H$_4$)]$^-$ species is shown in Fig. 1. The available infrared and all observed FT-Raman bands of [PdCl$_3$(C$_2$H$_4$)]$^-$ and the deuterated anion are tabulated in Table 2. The detection of CH stretching modes is very difficult in the case of tetra-alkylammonium salts in dichloromethane solution. After subtraction of cation and solvent bands three weak Raman bands have been observed at 2937, 2876 and 2850 cm^{-1}. These frequencies are rather low, but no other

Table 4
Correlation between frequency shifts of C=C stretching and CH$_2$ scissoring modes (Δv) and averaged metal–ethylene stretching force constants and frequencies

	Pd(C$_2$H$_4$)$^-$	[PtBr$_3$(C$_2$H$_4$)]$^-$	[PtCl$_3$(C$_2$H$_4$)]$^-$	PdCl$_3$(C$_2$H$_4$)]$^-$
Δv (cm^{-1})	240	219	210	171
K(MC$_2$) (N cm^{-1})	1.71	1.70	1.67	1.19
$\bar{v}$(MC$_2$) (cm^{-1})	(457) [a]	452	445	396

[a] The value in parenthesis is taken from DFT calculation.

spectral features were detected. In accordance with the DFT calculations and the Pt-analogue [5] the following assignments can be suggested: b_2 and a_2 for 2937 cm^{-1} and a_1 and b_1 for the other two bands, respectively. The C=C stretching mode was observed at 1526 cm^{-1} which shifted to 1380 cm^{-1} on deuteration and the CH_2 scissoring, to which is intimately coupled, shifted from 1267 to 929 cm^{-1} on deuteration. The CH_2 wagging and rocking modes were observed in positions rather close to those in Zeise's salt [5]. Both calculations (DFT and NCA) have fully supported our earlier assignment [5] for skeletal modes below 500 cm^{-1}. It is rather surprising that the Pd–ethylene tilt and symmetric stretching modes are very weak both in the IR and Raman spectra.

The experimental and calculated modes of $[PdCl_3(C_2D_4)]^-$ anion are collected and assigned in Table 2. According to the isotope sensitivity of vibrations related to C_2D_4 ligand, the C=C stretch, PdC_2 tilt, PdC_2 symmetric stretch and PdC_2 rocking modes can be easily assigned. Our assignments proposed in Table 2 show good agreement with the results of DFT calculations.

In order to perform the NCA analysis, the optimised geometry obtained for $[PdCl_3(C_2H_4)]^-$ was used, as no experimental structure data yet exist. The calculated force constants (Table 3) also confirm the lower stability of the Pd-analogue complex (higher CC stretching and lower PdC_2 stretching force constants) as compared to Zeise's salt. This is surprising since r(CC) is greater for Pd than for Pt.

The relative strength of the metal–ethylene bond can be characterised by the sum of the shifts in the coupled C=C stretching (a_1) and CH_2 scissoring (a_1) modes of co-ordinated ethylene as compared to those of gaseous ligand (1623 and 1343 cm^{-1}, respectively). The sum of the frequency shifts ($\Delta\nu$) shows the same trend as the metal–ethylene force constants (Table 4). It was obtained that the averaged frequencies of the metal–ethylene stretching modes, $\bar{\nu}(MC_2)$, serve as a measure of the strength of metal–ligand bonding. All these values are collected in Table 4.

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