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Bonding Properties of *trans*-$PtCl_2XY$ (X = C_2H_4; CO; Y = 4-R-Py). I. Infrared and Raman Spectra

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The infrared and Raman spectra of trans-$PtCl_2XY$ (X = C_2H_4; CO; Y = 4-R-Py) are presented. Variation of R has no influence on ν(C=C) of C_2H_4, the Pt–ethylene and the Pt–carbonyl frequencies and just a small influence on ν(CO).

On the other hand, ν(Pt–N) is strongly dependent on R and has a minimum value for R = H. This effect is explained in terms of the σ- and π-bonding properties of the 4-R-pyridines and the ionization potentials of platinum.

Introduction

In the complexes *tr*-$PtCl_2X$(4-R-Py), variation of R is expected to influence mainly the bonding between Pt and 4-R-Py, but also by its *trans*-effect the Pt–X bond. A much smaller *cis*-effect is expected for the Pt–Cl bond. Information about these effects can be obtained from X-ray results and from various spectroscopic techniques, such as NMR, NQR, infrared, Raman and UV.

Here we report our investigation of the Raman and infrared spectra of both *tr*-$PtCl_2(C_2H_4)$(4-R-Py) and *tr*-$PtCl_2$(CO)(4-R-Py) and the interpretation of these results in terms of the properties of the Pt–ligand bond.

The infrared spectra between 30–550 cm^{-1} for most of the ethylene compounds have been studied by Fritz and Sellmann[1]. Schmidt and Orchin[2] studied the R-dependence of ν(C=C) and ν(CO) for several complexes.

Our study is a more complete vibrational treatment of these complexes between 100–2000 cm^{-1} with the use of both infrared and Raman spectroscopy. Raman spectra of these complexes are reported for the first time.

Experimental

The compounds *tr*-$PtCl_2(C_2H_4)$(4-R-Py) were prepared by standard methods[2]. The compounds *tr*-$PtCl_2$(CO)(4-R-Py) were all prepared from their corresponding ethylene analogs[3].

All the ethylene complexes were yellow, the carbonyl compounds were yellow–green. The *tr*-$PtCl_2(C_2H_4)$(4-R-Py) complexes are fairly stable (Table I). On the other hand, the solid compounds *tr*-$PtCl_2$(CO)(4-R-Py) had to be kept at 0° C, because they slowly decomposed at room temperature. They are extremely water sensitive.

TABLE I. Analysis Figures for *tr*-$PtCl_2X$(4-R-Py).

X = C_2H_4	%C		%H		X = CO	%C		%H	
	calc.	exp.	calc.	exp.		calc.	exp.	calc.	exp.
R = NH_2	21.65	21.74	2.60	2.36	R = CH_3	21.71	21.62	1.81	1.57
CH_3	24.81	24.80	2.86	2.92	H	19.30	19.33	1.34	1.25
C_2H_5	26.93	27.18	3.27	3.35	Cl	17.67	17.99	.98	.88
CH_2OH	23.82	24.16	2.70	2.79	Br	15.93	16.64	.88	.91
H	22.52	22.32	2.43	2.36	CN	21.11	21.56	1.00	.99
Cl	20.62	20.87	1.98	1.91					
Br	18.60	18.79	1.78	1.89					
$CO_2C_2H_5$	27.00	27.57	2.92	3.00					
COOH	23.02	22.93	2.17	1.98					
$COCH_3$	26.04	26.18	2.67	2.79					
CN	24.12	24.39	2.02	1.95					

TABLE II. IR and Raman Frequencies of *tr*-$PtCl_2(C_2H_4)(4\text{-}R\text{-}Py)$.[a]

R = NH_2		C_2H_5		CH_3		CH_2OH		H		Cl	
IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
				131sh				131sh			
129s		140s(134)	153s	133s(134)		139sh(131)		135s(140)	153m	132m(133)	
166m	156s			168s		167sh					
					185sh						
177s		177s(178)	173sh	(174)	194s	175s(180)		176m(176)			
191m	202w	199s(194)	201m(196)	190m(207)	199s(194)	199s(195)	198w(198)	201s(200)	207s(204)	191vs(191)	190m(186)
				205sh							203sh
214vs	221w	206s(207)	211s(209)	211s(213)	218sh(210)	209s(212)	208w(210)			225s(213)	228w(212)
285s		269s		292s(290)	292w	285m(291)	284m	238vs(240)	237w	266m(280)	
	332sh		333sh		334sh		330sh		332sh	324s(325)	
	338vs		340vs(340)p		340vs(340)p		338vs(339)		339vs(340)p		338s(340)p
343vs		348vs	345sh	348vs		348s	354s	343vs		354vs	354vw
387m	385s	382s	385s(387)p	387m	385s(386)p	388w	384m(386)	377w	377s(387)p	391m	394m(390)p
413m	412w	411m	398w		400m(404)	402w	396vw	446w	393w		
436m							403vw		418vw		
481m	481m	483m	477m(484)	479w	480m(483)	474w	476m(476)	470w	472m(483)	483m	488w(486)p
				500vs	503w	494m	491m			502vs	
							1253vs				
1259m	1261vs	1253m	1256vs(1256)p	1252m	1256vs(1254)p	1262m	1259vs(1255)	1260w	1261s(1256)p	1246m	1250s(1255)p
1520vs	1523w	1523w	1523w(1525)p	1517vw	1520m(1526)p	1519w	1523m(1524)	1524vw	1528w(1524)p		1523m(1524)p

[a] The solution data are in parenthesis. The underlined hands are internal ligand bands. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, p = polarised.

Infrared spectra were recorded with Beckman IR-7, IR-11 and IR-12 spectrophotometers and were calibrated with H_2O, CO_2 and CO. Raman spectra were obtained with a Coderg PH 1 spectrophotometer with dc detection. The 6471 Å line of a CRL $52Kr^+$ laser was used as the exciting line.

Raman spectra of the ethylene complexes had to be taken with the spinning cell as described by Kiefer[4] because of the photosensitivity of the compounds.

Infrared spectra were recorded for the solid compounds between 100–2000 cm^{-1} and in solution between 100–340 cm^{-1}.

Raman spectra were run for solids and CH_2Cl_2 solutions (dp measurements) from 100–2000 cm^{-1}.

Results

The Raman and infrared spectra are compiled in Table II, III and IV. For mutual comparison the Raman spectra of the solid compounds $PtCl_2(C_2H_4)(Py)$ and $PtCl_2(CO)(Py)$ are depicted in Figure 1. Until now Raman spectra have not been measured for these compounds, presumably because many of them easily decompose in the laser beam.

However, with the use of the spinning cell, decomposition could be avoided for most of these substances. Apart from the skeletal vibrations of the complexes, the spectra contain the internal vibrations of the ligands and some additional lattice vibrations for the solids. The internal vibrations of the ligands outside the region of the skeletal vibrations (> 500 cm^{-1}) have been omitted in Tables II and III with the exception of $\nu(C{=}C)$, $\delta(CH)$ and $\nu(CO)$. The metal ligand vibrations, together with related modes as $\nu(C{=}C)$, $\nu(CO)$ and $\delta(CH)$ are compiled in Table IV.

When possible, data from solutions were used for the assignment. These assignments will be discussed in more detail.

$\nu(C{=}C)$ and $\delta_{symm}(CH)$ of Ethylene

It has been shown by Hiraishi[5] and Powell[6] that $\nu(C{=}C)$ and $\delta_{symm}(CH)$ are strongly coupled to each other.

For Zeise's salt ($KPtCl_3(C_2H_4)\cdot H_2O$)[5] these modes give rise to two Raman bands at 1522 and 1241 cm^{-1}. For $\nu(C{=}C)$ a much stronger Raman band is expected than for $\delta(CH)$.

Powell[6] has shown that the relative intensities of these two bands are a measure of the mixing of these vibrations.

Just as for Zeise's salt[5], all our ethylene complexes show a strong Raman band at about 1256 cm^{-1} and a much weaker band at about 1524 cm^{-1}. A high contribution of $\nu(C{=}C)$ to the lower frequency band is assumed for our complexes.

This conclusion is supported by the fact that a replacement of Cl^- by pyridine in going from Zeise's salt to *tr*-$PtCl_2(C_2H_4)(Py)$ shifts the 1241 cm^{-1} band to 1256 cm^{-1}, but the 1522 cm^{-1} only to 1524 cm^{-1}.

It may be seen from Table IV that variation of R has hardly any influence on $\nu(C{=}C)$.

$\nu(Pt\text{–}C_2H_4)$

For the bonding between Pt and C_2H_4 it is assumed, in agreement with the Chatt–Dewar[7,8] model, that Pt

Br		$CO_2C_2H_5$		COOH		$COCH_3$		CN	
IR	R	IR	R	IR	R	IR	R	IR	R
126m				132sh		131s		132sh	
136s(128)		141s(143)		139s(137)		136sh(130)		137s(131)	
		162w(165)	155m	147sh	155s	156m(165)	153s	167s(159)	
185vs(178)	182m(174)	183s(191)		188s(184)		189s(190)		195m(195)	
192sh(186)			(200)			197s		201sh(202)	206vs(205)
		203sh(214)							
220s(207)	222m(210)	209s(222)	240w	208s(211)		(209)	(208)	205s	221w
		(295)sh	300w	261s		252m(242)		254m(254)	
253m(262)	255w	297m(279)	269w	269s(284)		262m(278)			
301m(301)			335s(338)p	302s(302)	334sh	308w(304)	327sh		331sh
331w	334s(339)p		341vs(341)p		340s(336)p		334vs(339)p		337vs(340)p
352s	350m	347vs	350m	347s	353w	345vs	344m	352vs	351m
371w	373vs(372)p								
400m	402s(399)p	387m	388s(386)p	380m	380m(385)p	377m	385s(380)p	381m	381s(385)p
					390w	402w	(396)p		
	431w	421vw	425vw	428vw	425vw(422)p		427vw(422)p	397w	398w
				466m	466m				
476w	487m(486)	478w	475m(480)	478sh	482vw(480)p	480w	476m(479)	475w	475m(482)
491s					1255s				
1255w	1252vs(1256)p	1254m	1255vs(1256)p	1251vw	1259s(1257)p	1254w	1258s(1256)p	1260vw	1260s(1256)p
	1524w(1524)	1521vw	1520m(1520)	1519w	1522m(1524)p	1520vw	1522m(1524)p		1522m(1523)p

is bonded to both carbon atoms forming a three membered ring[5]. There are two Pt–C$_2$ stretching vibrations, symmetric and antisymmetric respectively, for which the assignment is straightforward from depolarization measurements. For Zeise's salt and $[PtCl_2(C_2H_4)]_2$ these vibrations are found at about 400 and 490 cm^{-1}. All our C_2H_4 complexes show two bands at about 385 and 480 cm^{-1} respectively, which are not present in the spectra of the corresponding *tr*-PtCl$_2$(CO)(4-R-Py) and *tr*-PtCl$_2$(4-R-Py)$_2$[9,10] complexes. The lower frequency band is strong in the Raman and polarized and therefore assigned to the symmetrical stretch; the higher frequency one is weaker and depolarized (ν_{as} (Pt–C$_2$)). This assignment is opposite to the one given by Fritz and Sellmann[1] on the basis of their infrared measurements.

Comparing these results with the frequencies of Zeise's salt (404 and 492 cm^{-1}) we may conclude that our Pt–ethylene bond is somewhat weaker because of the stronger *trans*-influence of the pyridine group. This is also reflected in the higher value of ν(C=C) in our complexes with respect to Zeise's salt (1241 cm^{-1}).

Again it may be seen from Table IV that variation of R hardly influences either Pt–C$_2$ vibration.

ν(Pt–CO) and δ(Pt–CO)

Comparing the frequency region of the skeletal modes for the carbonyl and ethylene compounds, three more bands appear in the infrared spectra of the carbonyl complexes at about 480, 512 and 545 cm^{-1} (the band at 480 cm^{-1} in the ethylene compounds belongs to the ν_{as}(Pt–C$_2$)).

Three Pt–carbonyl vibrations are expected for a C_{2v} point group, considering the pyridine ligand as a single atom: two Pt–CO bending modes (B_1 and B_2) and one Pt–CO stretching vibration (A_1), all modes being IR allowed and Raman active. There is not much agreement in the literature about the assignment of these bands. Gribov *et al.*[11] discussed these bands in *cis*- and *trans*-PtCl$_2$(CO)(NH$_3$). They assigned the 530 cm^{-1} and the 480 cm^{-1} bands to deformation vibrations of the Pt–carbonyl group. Denning and Ware[12] investigated KPtCl$_3$(CO) and assigned the 530 cm^{-1} band to ν(Pt–CO) and the 480 cm^{-1} band to δ(PtCO), because of the polarization of the 530 cm^{-1} band. Recently Cleare and Griffith[13] have also studied the $[PtCl_3(CO)]^-$ ion. They gave the opposite assignment for the bands on the basis of the intensities and state of polarization in the Raman spectra. This assignment is in agreement with a study by Adams[14] of carbonyl complexes, in which δ(MCO) has always been found at higher frequency than ν(M–CO). In the Raman spectra of our solutions only one rather strong, polarized band is found at 480 cm^{-1}. Thus, our data support the assignment of Cleare and Griffith, and we assign the 480 cm^{-1} band to ν(Pt–CO) (A_1). In that case the 512 and 545 cm^{-1} bands have to be the δ(PtCO)'s.

ν(CO)

In the infrared carbonyl stretching region two bands are found for the solids (Table III), a strong band at higher frequency and a weak one. Both bands are also found in solution and the frequency difference of 55 cm^{-1} is in accordance with the assignment of the

TABLE III. IR and Raman Frequencies of *tr*-$PtCl_2(CO)(4\text{-}R\text{-}Py)$.[a]

R = CH_3		H		Cl		Br		CN	
IR	R	IR	R	IR	R	IR	R	IR	R
	103m				109m		105m		
		128s	117m	129vs				128sh	
126vs (130)	114m	137sh (129)	133m	136sh (126)	137m	128s		131vs (130)	120sh
	146m	160s				150m			
159s (160)	154s	163sh (157)	161s	157s (156)		168m	148sh	156vs (155)	150m
197m (198)	198w		190w	188s (186)		175m			
	214w (222)p	226m (221)	226m					217s (227)	
277m (285)	269w			274s (275)	270w	262m	261m	240m (267)	246m (246)
				329m (326)		295s	297m	300w (304)	
	332sh		336sh		335sh		330sh		332sh
339sh	339vs (344)p		342s (344)p		340vs (344)p		336vs	340sh	342vs (342)p
351s	354s	354s	353sh	356s	352vw	355s	352w	356vs	360s
364m	365w	436s				384w	382s	401w	
486vs	483sh			488s	498m (492)	485s			
			474m					475w	
494sh	490s (478)p	479m	480m (476)p	461m	460s (460)p	498sh	492s	497m	478s (472)p
513s	515w	509s	510vw	515s		512s	510w	534vs	
548s		542s		548s		548s		548m	
2059sh (2079)		2067sh		2064m		2066m		2070sh (2089)	
			2121w						
2116vs (2130)	2122 (2131)p	2121vs	2131w (2126)	2123vs	2127m (2133)p	2120vs	2130	2126vs (2137)	2133m (2138)p

[a] The solution data are in parenthesis. The underlined bands are internal ligand bands. vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, p = polarised.

TABLE IV. Assignment of Bands to the Vibrations which are Most Sensitive to Metal–Ligand Interactions (in approximate description).

Assignment	*tr*-PtCl$_2$(C$_2$H$_4$)(4-R-Py)											*tr*-PtCl$_2$(CO)(4-R-Py)				
	R – NH$_2$	C$_2$H$_5$	CH$_3$	CH$_2$OH	H	Cl	Br	CO$_2$C$_2$H$_5$	COOH	COCH$_3$	CN	CH$_3$	H	Cl	Br	CN
ν(Pt–N)	285^a	269^a	290	291	240	280	262	279	284	278	254	285	221	275	262^a	267
ν_s(Pt–Cl)	338^a	340p	340p	339	340p	340p	339p	341p	336p	339p	340p	344p	344p	344p	341p	342p
ν_{as}(Pt–Cl)	343^a	348^a	348^a	348^a	343^a	354^a	352^a	347^a	347^a	345^a	352^a	351^a	354^a	356^a	355^a	356^a
ν_s(Pt–C$_2$)	385^a	387p	386p	386	387p	390p	399p	386p	385p	380p	385p					
ν_{as}(Pt–C$_2$)	481^a	483^a	479^a	474^a	470^a	483^a	476^a	478^a	466^a 478^a	480^a	475^a					
ν_s(Pt–CO)												478p	476p	460p	492^a	472p
δ(PtCO)												513^a	509^a	515^a	512^a	534^a
δ(PtCO)												548^a	542^a	548^a	548^a	548^a
ν(C = C)	1261^a	1256p	1254p	1255	1256p	1255p	1256p	1256p	1257p	1256p	1256p					
δ(CH)	1523^a	1525p	1526p	1524	1524p	1524p	1524	1520	1524p	1524p	1523p					
ν(CO)												2131p	2126p	2133p	2130^a	2138p
σ_p^{b}	–.66	–.15	–.17	+.10^c	0	+.23	+.23	+.45	+.45	+.50	+.66	–.17	0	+.23	+.23	+.66

^{a} These data are from the solid. p = polarised. ^{b} σ_p is the Hammett parameter. Values from C.G. Swain and E.C. Lupton, *J. Am. Chem. Soc., 90,* 4328 (1968). ^{c} from ref. 4.

weaker band to ν(^{13}CO). This isotope band has also been found by Kong and Theophanides[15] for *tr*-Pt(CO)(8-hydroxyquinolinato)Cl. The Raman spectra show a polarized band for this vibration at about 2130 cm^{-1}.

The position of ν(CO) in CH$_2$Cl$_2$ solution moves slightly to higher frequency in going to a more electron-withdrawing substituent in the pyridine ring. *tr*-PtCl$_2$(CO)(4-Br-Py) disagrees with this order, but for this compound we had to use results for the solid because of low solubility.

ν(Pt–Cl)

Two such vibrations are expected to appear for both C$_2$H$_4$ and CO complexes in the frequency region 300–350 cm^{-1} according to the results for other *tr*-PtCl$_2$XY complexes[16, 17]. Because of the presence of a centre of symmetry for the Cl atoms, an alternation of intensity for IR and Raman is expected for the symmetric and antisymmetric Pt–Cl stretching modes. In fact for most complexes a strong, polarized band is found in the Raman spectra at about 340 cm^{-1}, which can be assigned to ν_s(PtCl). The expected isotope splitting is found for nearly all complexes in the solid state spectra. The antisymmetric vibration, which is normally found as a weak band or shoulder in the Raman, is strong in the infrared at about 348 cm^{-1}.

The frequency values of both vibrations show only small irregular changes on varying R in the pyridine ring. Thus, the cis effect is very small. This may also be concluded from the ^{35}Cl NQR frequencies which have been recorded for the C$_2$H$_4$ complexes[30].

For all the complexes the frequency value is about 21.2 Mhz. Until now no NQR signals could be recorded for the carbonyl complexes.

ν(Pt–N)

For many pyridine complexes[18], the M–N stretching vibration has been identified between 200 and 300 cm^{-1}. The IR spectra of all our complexes, CO as well as C$_2$H$_4$, show a strong band in this region, not found in the infrared spectra of *e.g.* Zeise's salt[1] and *tr*-PtCl$_2$(C$_2$H$_4$)(NH$_3$), but present in the infrared spectra of *tr*-PtCl$_2$(4-R-Py)$_2$[9, 10] and KPtCl$_3$(Py)[19]. It is the only vibration which is really dependent on the nature of R and is therefore assigned to ν(Pt–N). In agreement with the results for PtCl$_2$(4-R-Py)$_2$, this vibration cannot normally be detected in the Raman spectra because of the low polarizability of the Pt–Py band. It appears from the infrared spectra that this vibration especially shifts appreciably in going from solution to the solid state. Normally the frequency is lowered, presumably because of intermolecular interactions via the R group of pyridine in the solids. Therefore, frequency values for the compounds in solution are used in our assignment and discussion of the results in the next section.

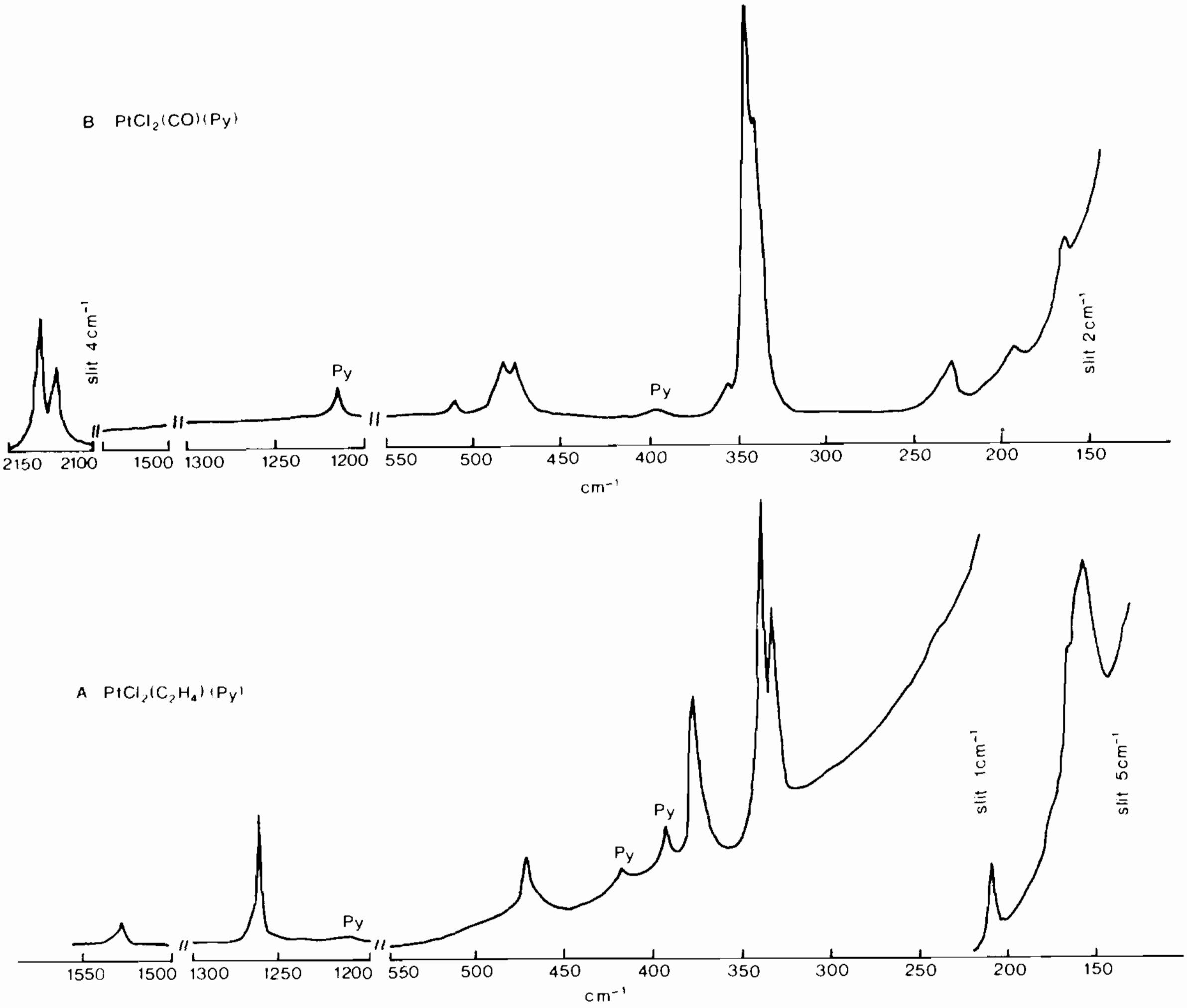

Figure 1. Raman spectra of *tr*-$PtCl_2(C_2H_4)(Py)$ (A) and *tr*-$PtCl_2(CO)(Py)$ (B) for the solid compounds.

Skeletal Deformation Modes

All these deformation modes are found in the region 120–210 cm^{-1}. Assignment of these vibrations is difficult.

They all lie close together in a small frequency range and may coincide and couple with lattice modes. Besides, no reliable depolarization measurements can be made for the lower frequency bands. However, for some of these modes, the assignment is reliable. All *tr*-$PtCl_2XY$ complexes, so far investigated[10, 12, 20] show two bands in the infrared and Raman spectra at about 130 cm^{-1} and 160 cm^{-1} respectively, which are not found in the corresponding *tr*-$PtBr_2XY$ complexes[10]. They are therefore assigned to the Pt–Cl deformations. These bands are not dependent on R.

Another band for which the assignment is straightforward is found at about 205 cm^{-1} in the Pt–C_2H_4 complexes. It is not present in the CO complexes and in the *tr*-$PtCl_2(4\text{-}R\text{-}Py)_2$, but also found for Zeise's salt. Therefore, this band is assigned to a Pt–C_2 deformation mode.

Discussion

The most important result from the vibrational spectra, as seen from Tables II, III and IV is the manner in which ν(Pt–N) depends on R. However, before we discuss these results, we have to consider the coupling of ν(Pt–N) with other skeletal modes.

It appears from the spectra that variation of R only affects the position of ν(Pt–N) without any regular shift for ν_s(Pt–C_2) and ν_s(Pt–Cl). Such regular shifts would have to occur if a strong coupling between these modes existed, just as in the case of ν(C=C) and δ(CH).

Since the mass changes are small in the 4-R-Py series, with the exception of R = Br and $CO_2C_2H_5$, the frequency change of ν(Pt–N) with R is mainly due to a change in the strength of the Pt–N bond. This conclusion is in accordance with the result of Wong and Brewer, that the magnitude of the metal–pyridine stretching frequency may be used as a measure of the coordination bond strength between copper and pyridine[21–24].

The dependence of ν(Pt–N) on R is shown in Table IV. It is clear that this vibration does not change in the same way as the basicity or Hammett σ_p parameter of R. In this respect our results differ from the data given by Fritz and Sellmann[1] for these compounds. The result is not surprising, since the basicity is derived purely from the protonation of N without taking into account the π-bonding property of pyridine.

In fact, the strength of the Pt–Py bond is determined by both σ- and π-bonding properties of Pt and pyridine.

In going from R = CH_3 to R = H the σ-bond strength decreases, while the π-bonding is of much less importance here. As a consequence ν(Pt–N) is lowered. On going from R = H to R = CN, the σ-bond further decreases, but this effect is now compensated by a strengthening of the π-bond with an accompanying increase of ν(Pt–N). As a result a minimum for R = H in ν(Pt–N) is found in both CO and C_2H_4 complexes.

This behaviour is strongly reminiscent to the observations made for the case of the equilibrium studies[25]:

$$\begin{aligned} &CH_3(CH_2)_9CH{=}CH_2 + (C_6H_5CH{=}CH_2)PtCl_2 \\ &\quad (4\text{-R-PyO}) \rightleftharpoons (CH_3(CH_2)_9CH{=}CH_2)PtCl_2 \\ &\qquad (4\text{-R-PyO}) + C_6H_5(CH{=}CH_2) \end{aligned}$$

for which a minimum value of K_{eq} has been found for R = H. The irregularity of the increase of ν(Pt–N) from R = H to R = CN is caused by the difference between the decrease in σ-bonding ability and the increase in π-bonding ability for the various substituents. The extreme low σ-bonding ability for R = CN is responsible for the rather low value of ν(Pt–N).

The same dependence of the ν(M–N) frequency and R as observed for our complexes, has been found for the $ZnCl_2$(4-R-pyr)$_2$ complexes. On the other hand, a correlation between ν(M–N) and Hammett σ_p parameter has been observed for the $CuCl_2$(4-R-pyr)$_2$[21–24]. Wong and Brewer explained this behaviour by the strong σ-bonding ability of Cu, while for Zn the σ- and π-bonding properties are weaker and of more equal importance. They related this behaviour to the 1st and 2nd ionization potentials (IP) of the metal. Considering the IP's of Pt (9.000 and 18.56eV) in connection with those of Cu (7.724 and 20.29eV) and Zn (9.391 and 17.96eV) we see that the IP's of Pt are close to those of Zn[26]. Thus, our relation between ν(Pt–N) and R is not in disagreement with the explanation given by Wong and Brewer. Recently, Pfeffer *et al.*[10] investigated the IR and Raman spectra of *tr*-$PtCl_2$(4-R-Py)$_2$.

They also found the irregular dependence of ν(Pt–N) on R as recorded for our complexes, but they gave no sound explanation for this effect.

A subject of our further investigation will be the influence of *trans* ligands other than CO and C_2H_4, on the bond strength dependence on R for the Pt–4-R-Py bond. The *trans* influence of the variation of R on C_2H_4 and CO can easily be understood in terms of the σ- and π-bonding properties of the pyridine-group. In going from R = H to R = CH_3, the Pt–Py σ-bond will be strengthened and the π-bond weakened. The reverse will hold for the Pt–C_2H_4 and Pt–CO bond, and variation of R has two opposite effects on these bond strengths. Especially when these effects are small (which is the case when a substituent in a ring is varied) only very small shifts of ν(Pt–C_2) and ν(Pt–CO) would be expected. Because of the smallness of these effects nothing can be concluded about the relative importance of the σ- and π-bond between Pt and ethylene. Further ν(C=C) does not change, because this vibration also undergoes the influence of two weak, opposite effects. On the other hand, a change in the Pt–Py σ-bond has much less influence on the C≡O bond, because the lone pair of carbon is mainly used in the Pt–CO σ-bond. The accompanying change in the Pt–Py π-bond however affects the C≡O bond. Therefore the *trans*-influence of R is only manifested in a shift of ν(CO) in such a way that variation of R from R = CH_3 to R = CN causes an increase of ν(CO). The lowering of ν(CO) with regard to free CO in these complexes is only about 10 cm^{-1}.

However, this does not mean that π-bonding between Pt^{2+} and CO is negligible in this case. In pure σ-complexes, such as H_3B–CO[27], ν(CO) is raised with respect to the free CO ligand from 2143 to 2164 cm^{-1} (compare also the value of ν(CO) for CO adsorbed on ZnO at 2210 cm^{-1})[28]. Thus, we do not agree with the statement of Brause *et al.*[3] that π-bonding is not important for *tr*-$PtCl_2$(CO)(4-R-Py) complexes. On the other hand, π-bonding is much weaker here than in many other transition metal–CO complexes. Comparing *e.g.* the values for ν(CO) in the CO complexes $KPtCl_3CO$[12] and *tr*-Ir(CO)Cl$(PPh_3)_2$[29], we find a much higher frequency in $KPtCl_3CO$ (2126 cm^{-1}) than in Vaska's compound of the isoelectronic Ir^+ (1967 cm^{-1}).

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