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Bonding Properties of *trans*-$PtCl_2XY$ (X = C_2H_4; CO and Y = 4-R-Py). II. Electronic Absorption Spectra

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The electronic absorption spectra of tr-$PtCl_2XY$ (X = C_2H_4; CO and Y = 4-R-Py) are presented. Two bands are found in the UV, the frequencies of which are both dependent on R. The highest energy band is assigned to the $\pi \rightarrow \pi^*$ transition of the pyridine ligand, the other to an inverse charge transfer (CT) transition between platinum and the pyridine ligand.

Introduction

The influence of the variation of R on the properties of the above complexes has been investigated by different spectroscopic techniques *e.g.* IR, Raman[1], UV and NMR.[2] Our interest in the UV absorption spectra which have been recorded for the first time, originated from our NMR results[2]. Comparison of our spectra with those of *tr*-$PtCl_2(4\text{-R-Py})_2$[3] *tr*-$PtCl_2(NH_3)(C_2H_4)$ and $KPtCl_3(C_2H_4)\cdot H_2O$[4,5] assisted in the assignment of the bands.

Experimental

The compounds *tr*-$PtCl_2(C_2H_4)$(4-R-Py) were prepared by standard methods[6]; the *tr*-$PtCl_2$(CO)(4-R-Py) were synthesized from their corresponding ethylene analogues[7]. See ref. 1 for the analytical data.

The UV spectra were recorded on a Cary 14 spectrophotometer. Extinction coefficients were determined in CH_2Cl_2. Diffuse reflectance spectra were recorded for all compounds. The ε values for *tr*-$PtCl_2$(CO)(4-Cl-Py) and *tr*-$PtCl_2$(CO)(4-Br-Py) are not very reliable, because these compounds slowly decompose. The spectra of the ethylene compounds were analyzed on a Du Pont type 310 curve resolver. The spectra of the CO complexes could not be resolved in this way owing to extensive overlapping of absorption bands.

For some compounds spectra were recorded at 77° K, which however did not yield additional information.

Results and Discussion

The Ethylene Complexes

The energies and intensities of the absorption bands are presented in Table I. The spectra of the complexes in solution are similar to the spectrum given in Figure 1.

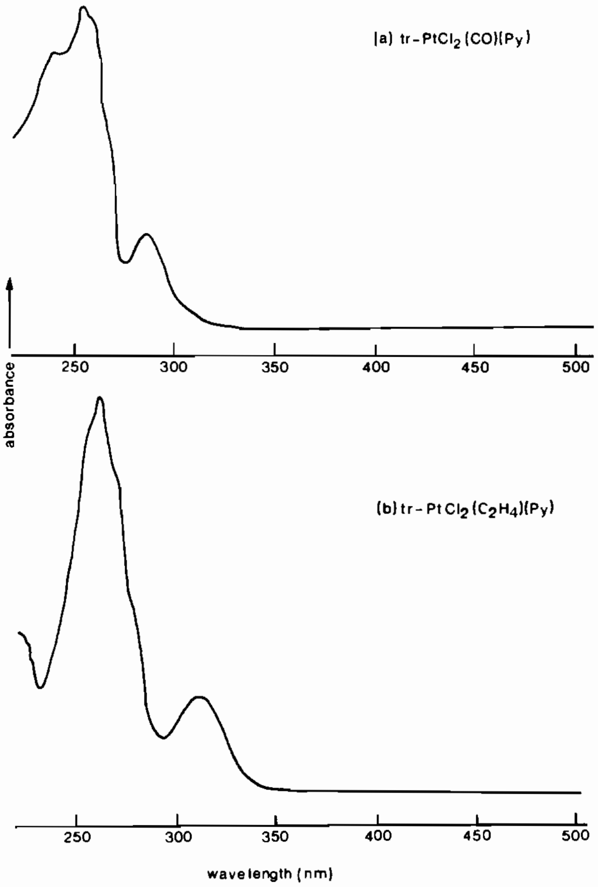

Figure 1. UV spectra of *tr*-$PtCl_2$(CO)(Py) (a) and *tr*-$PtCl_2(C_2H_4)$(Py) (b) in CH_2Cl_2 solution.

TABLE I. UV Spectral Results for *tr*-$PtCl_2(C_2H_4)$(4-R-Py) (energies in kK). The values of ε_{max} in CH_2Cl_2 are given in brackets. The bands below the solid line are only found in the diffuse reflectance spectra and represent singlet–triplet *d–d* transitions.

R = NH$_2$	CH$_3$	C$_2$H$_5$	CH$_2$OH	H	Cl	Br	CO$_2$C$_2$H$_5$	COOH	COCH$_3$	CN	Assignment
38.76	38.31(3640)	38.31(3860)	38.17(5260)	38.17(3825)	37.66(4070)	37.59(6200)	35.65(4410)	35.59(4980)	35.31(4860)	35.34(5000)	$\pi\rightarrow\pi^*$
36.36											
32.52	32.15(1060)	32.34(900)	32.12(1000)	32.03(925)	31.85(985)	31.75(1165)	31.70(1500)	30.94(930)	30.94(1190)	30.96(1475)	$d(Pt)\rightarrow\pi^*$
29.4	27.5			28.2				28.5	27.2		$d\rightarrow d$
		26.3	26.6		26.5	25.9	26.2				
26.4	24.1			25.0				25.8	24.6	24.6	$d\rightarrow d$
22.7	22.1	22.6	22.4	22.3	22.3	22.4	23.4	22.5	21.3	21.9	$d\rightarrow d$
			18.1								$d\rightarrow d$

Only two distinct absorption bands are observed in the ultraviolet region. The band at about 36–37 kK is also found in the spectra of the free pyridine ligands, at the same position and with the same intensity ($\varepsilon \simeq 4000$) and vibrational structure. This hand is therefore assigned to the $\pi\rightarrow\pi^*$ transition of the 4-R-Py ligand in the complex. Similar bands occur in many other metal–pyridine complexes[3,8,9,10] and are also found in the carbonyl complexes which are discussed here (Table III). However, a coincidence with other transitions is possible because both *tr*-$PtCl_2(NH_3)(C_2H_4)$ and *tr*-$PtCl_2(NH_3)_2$[3] possess an absorption band in this region, which has been assigned to $5d(Pt)\rightarrow\pi^*(C_2H_4)$[4] and $d\rightarrow d(Pt)$[3] transitions respectively. The other absorption band at about 32 kK, which is too intense ($\varepsilon \simeq 1000$) to be assigned to a *d–d* transition, depends strongly on the R substituent in the pyridine ring (Table I).

A CT transition between Pt and Py is therefore the most likely explanation. Variation of R from an electron releasing (*e.g.* NH_2) to an electron withdrawing (*e.g.* CN) substituent in the pyridine ring causes a shift of this band to lower energies just as for the corresponding *tr*-$PtCl_2$(4-R-Py)$_2$[3] and $[Ru(NH_3)_5$(4-R-Py)$]^{2+}$ [10] complexes.

This behaviour and the fact that these bands are not found in the spectra of the Pd complexes[11] can only be explained by an assignment of these bands to inverse charge transfer ($5d(Pt)\rightarrow\pi^*(Py)$) transitions.

The shift to lower energies is then explained by a lowering of the π^* lewel of 4-R-Py in going from R = NH_2 to R = CN. The inverse CT transition may originate from more than one *d* level of Pt and for the *tr*-$PtCl_2$(4-R-Py)$_2$[3] complexes three such transitions have indeed been found. However, for our complexes only one transition could be detected. The other transitions coincide with other bands of the complex. Just as for the *tr*-$PtCl_2$(4-R-Py)$_2$ complexes this lowest energy transition originates from the $5d_{xy}(Pt)$ level (x and y are axes in the molecular plane, Figure 2), which level

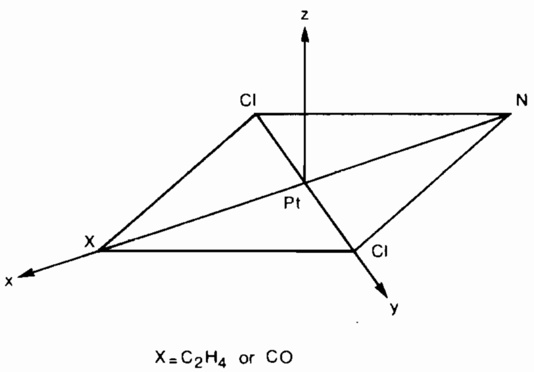

Figure 2. Coordinate system and geometry of the *tr*-$PtCl_2X$ (4-R-Py) complexes.

is of course sensitive to changes of the ligands in the complex. Thus, a replacement of Cl by Br makes the $5d_{xy}$ level more anti-bonding in character, which causes a red shift of 500 cm^{-1} for the $5d_{xy}(Pt)\rightarrow\pi^*$ transition (Table II).

The Carbonyl Complexes

The *tr*-$PtCl_2(CO)$(4-R-Py) complexes have been studied in the same way. Both $\pi\rightarrow\pi^*$ and inverse CT transitions are also present in these spectra. The $\pi\rightarrow\pi^*$ band is more complex here and the CT band is shifted to higher energies with respect to the ethylene analogues (Table III). This latter shift can be explained by comparing the bonding properties of the respective complexes. Both C_2H_4 and CO form σ- and π-bonds with Pt. The σ-bond is formed for both ligands with the empty $5d_{z^2}$, $5d_{x^2-y^2}$, $6s$, $6p_x$ hybrid orbital (see Figure 2) of platinum. Different Pt orbitals however are used for the π-back bonding from Pt to CO and C_2H_4 respectively. In the most stable configuration of the ethylene complexes[12,13] C_2H_4 is positioned perpendicular to the molecular plane. Therefore, π-back bonding from Pt to C_2H_4 takes place by overlap of the Pt $5d_{xz}$, $6p_z$ hybrid orbital with the π^* level of C_2H_4. As a consequence, the $5d_{xy}$ level of Pt and also the $5d_{xy}\rightarrow\pi^*$ CT transition is not much affected by the π-back bonding to C_2H_4.

On the other hand, π-back bonding from Pt to CO takes place from both Pt $5d_{xz}$, $6p_z$ and $5d_{xy}$ orbitals to the degenerate π^* level of CO. The Pt $5d_{xy}$ level will be lowered in energy by this interaction and the $5d_{xy}\rightarrow\pi^*$ CT transition will be higher in energy than the corresponding transition in the ethylene analogue (Table III).

TABLE II. Transition Energies (in kK) of $d(Pt)\rightarrow\pi^*$ in $PtX_2(C_2H_4)$(4-R-Py). Values from solutions in CH_2Cl_2.

R	X = Br	X = Cl	ΔE
CH_3	31.65	32.15	0.50
H	31.55	32.03	0.48
Br	31.25	31.75	0.50

Replacement of C_2H_4 by CO may also influence the effective charge on Pt and, as a consequence, the energy of the CT transition. This however is only a secundary effect. An almost constant difference in CT energies is found between the CO and analogous C_2H_4 complexes (about 2.9 kK) except for 4-CN-pyridine (1.4 kK, Table I and III).

The 4-CN-pyridine ligand is a very strong π-acceptor, while CO, but not C_2H_4, is a weak π-acceptor in Pt^{II} complexes (ν(CO) is only lowered about 10 cm^{-1} with respect to the free ligand).

The π-bond between Pt and CO will even be more weakened by the strong π-acceptor properties of the 4-CN-pyridine ligand and as a result the $5d_{xy}$ orbital will be less affected in this complex than in the other CO compounds. Therefore, the energies of the $5d_{xy}\rightarrow\pi^*$ CT transitions of the Pt–C_2H_4 and CO complexes of 4-CN-pyridine do not differ so much from each other as they do for the other pyridine complexes of C_2H_4 and CO.

Finally, we recorded the diffuse reflectance spectra for all these compounds in order to observe the *d–d* transitions of Pt, which are not found in the solution spectra. These data were compared with the results for related complexes K_2PtCl_4[14], $KPtCl_3(NH_3)$[15], $KPtCl_3(C_2H_4)$[4,5], *tr*-$PtCl_2(NH_3)_2$[3] and *tr*-$PtCl_2(Py)_2$[3]. Substituting Cl by NH_3 or Py causes an increase of the crystal field splitting energy Δ_1 of about 3.5 kK; substitution of Cl by C_2H_4 does increase the Δ_1 value by about 5 kK and a replacement of Cl by CO causes an increase in the Δ_1 of about 7 kK.

Taking into account these values, we made a tentative assignment for the diffuse reflectance bands (Table I and III).

The diffuse reflectance spectra of the CO compounds are not so reliable because sometimes the compound began to decompose during measuring the spectrum.

TABLE III. UV Spectral Results for *tr*-$PtCl_2(CO)$(4-R-Py) (energies in kK). The values of ε_{max} in CH_2Cl_2 are given in brackets. The bands below the solid line are only found in diffuse reflectance spectra and represent singlet–triplet *d–d* transitions.

R =	CH_3	H	Cl	Br	CN	Assignment
	41.8	39.1			38.2	
	39.4	38.3			36.0	
	37.7	37.3			34.8	
	35.09(1725)	34.97(1679)	34.84(~1400)	34.72(~1400)	32.36(1025)	$d(Pt)\rightarrow\pi^*$
	29.3	29.7	27.9	26.7	29.2	$d\rightarrow d$
	24.2	24.4	24.4	23.5	24.6	$d\rightarrow d$
	18.8	18.7	20.0	19.5	18.5	$d\rightarrow d$
	15.6	15.7	16.7	16.3	15.7	$d\rightarrow d$

Thus, it is possible that the low energy absorptions in the carbonyl compound (24.0, 19.0 and 16 kK) are due to decomposition of the complex.

Conclusion

The spectra in solution only show two absorption bands, which are assigned to a $\pi \rightarrow \pi^*$ transition of pyridine and an inverse CT transition from $5d_{xy}(Pt) \rightarrow \pi^*$ (pyridine) respectively. The CT absorption band shifts to lower energies when R is varied from NH_2 to CN. This result will be shown in a future publication to be of importance in the interpretation of the ^{13}C chemical shifts of these complexes[2].

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