

APPLICATION OF SPECTROSCOPIC TECHNIQUES TO SUBSTITUTED ANILINE DERIVATIVES OF ZEISE'S SALT

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ABSTRACT

The ^1H NMR, IR and electronic spectra are reported for a range of complexes *trans*- $[\text{PtCl}_2(\text{CH}_2=\text{CH}_2)(\text{R-an})]$ comprising fifteen variously-substituted anilines, R-an. The coupling constant, $J_{\text{Pt-H}}$, is approximately 64 Hz which is consistent with *trans* coordination. The chemical shift of the olefinic protons is relatively unaffected by variation of R but the shielding of the aromatic protons is slightly modified. All three infrared modes $\nu\text{Pt-C}_2$, $\nu\text{Pt-N}$ and $\nu\text{C-C}$ (olefin) are simultaneously increased by electron-releasing substituents showing that the electronic effects of R are transmitted throughout the complex molecule. The UV spectra show that the $\pi \rightarrow \pi^*$ transition within the aniline ring is the electronic band of maximum sensitivity to R.

INTRODUCTION

The chemistry of Zeise's salt, $\text{K}[\text{PtCl}_3(\text{CH}_2=\text{CH}_2)]$, has attracted much attention. Recently [1] we reported the IR and Raman spectra of the complexes *trans*- $[\text{PtX}_2(\text{CH}_2=\text{CH}_2)\text{L}]$ (L = pyridine *N*-oxide, aniline and imidazole) and have now turned our attention to the spectra (NMR, IR and UV) of a series of compounds *trans*- $[\text{PtCl}_2(\text{CH}_2=\text{CH}_2)(\text{R-an})]$ where R-an represents a wide range of variously-substituted anilines.

EXPERIMENTAL

The complexes were prepared by adding a concentrated ethanolic solution of the substituted aniline (1 mmol) to an ethanolic solution of Zeise's salt (1.2 mmol). The mixture was stirred overnight and the ethanol was allowed to evaporate until crystallization was essentially complete. The products were collected by filtration, washed with water and dried over silica gel under reduced pressure. Composition and purity were determined by microanalysis (C, H, N).

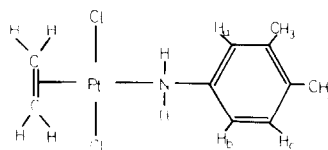
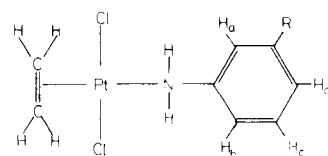
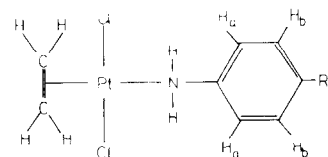
^1H -NMR spectra were run at ambient temperature on a Bruker WH-90 spectrometer using CDCl_3 as solvent and lock and tetramethylsilane (TMS) as reference. Infrared spectra were determined on nujol mulls (1700–1500

and 1300–300 cm^{-1}) or hexachlorobutadiene mulls (4000–1700 and 1500–1300 cm^{-1}) between CsBr plates on a Beckman IR-12 spectrophotometer and as nujol mulls between polyethylene plates (500–80 cm^{-1}) on a Digilab FTS 16 B/D interferometer. The UV spectra were determined on a Varian Superscan 3 spectrophotometer using CDCl_3 as solvent.

RESULTS AND DISCUSSION

NMR spectra

The ^1H NMR data referred to the following structures are recorded in Table 1. $J_{\text{Pt-H}}$ is relatively constant and its value is consistent with the NMR



data for analogous complexes in which the aniline is replaced by pyridine, pyrazine, imidazole, ammonia and pyridine *N*-oxide [2–6]. There is also little variation in the chemical shift of the olefin protons which are too far removed from the substituent for its shielding effect to be transmitted. A similar observation was made [7] for the complexes *trans*-[PtCl₂(CH₂=CH₂)(R-py)] (R-py = substituted pyridine). The chemical shifts of the aromatic protons tend to be higher for electron withdrawing substituents which clearly increase the electron density within the aromatic ring and hence the shielding of the aromatic protons.

Infrared spectra

The bands of primary interest which are most likely to be influenced by the substituent effects are $\nu\text{Pt-C}_2$ (antisymmetric and symmetric), $\nu\text{Pt-N}$

TABLE 1

¹H NMR data for the complexes *trans*-[PtCl₂(CH₂=CH₂)(R-an)]

R	σ	Olefin protons		Aniline protons	Other
		$J_{\text{Pt-H}}$ (Hz)	δ (ppm)	δ (ppm)	δ (ppm)
<i>p</i> -NO ₂	0.778	64	4.68	8.25(H _a) 7.58(H _b)	
<i>m</i> -NO ₂	0.710	64	4.65	Multiplet at 7.66(mean)	
<i>m</i> -Br	0.391	64	4.72	Multiplet at 7.36(mean)	
<i>m</i> -Cl	0.373	64	4.70	Multiplet at 7.34(mean)	
<i>m</i> -I	0.352	64	4.72	Multiplet at 7.38(mean)	
<i>m</i> -F	0.337	64	4.72	Multiplet at 7.20(mean)	
<i>p</i> -I	0.276	64	4.70	7.68(H _a) 7.15(H _b)	
<i>p</i> -Br	0.232	64	4.71	7.49(H _a) 7.28(H _b)	
H	0				
<i>p</i> -OC ₆ H ₅	-0.028	64	4.70	7.36(H _a) 6.96(H _b)	7.14 (OC ₆ H ₅)
<i>m</i> -CH ₃	-0.069	64	4.67	Multiplet at 7.20(mean)	2.36 (CH ₃)
<i>p</i> -t-C ₄ H ₉	-0.120	63	4.69	7.33(H _a) 7.33(H _b)	1.31 (t-C ₄ H ₉)
<i>p</i> -CH ₃	-0.170	64	4.66	7.28(H _a) 7.13(H _b)	2.31 (CH ₃)
3,4-di-CH ₃	-0.240	64	4.66	Multiplet at 7.20(mean)	2.20, 2.25 (CH ₃)
<i>p</i> -OCH ₃	-0.268	63	4.67	7.35(H _a) 6.85(H _b)	3.78 (OCH ₃)

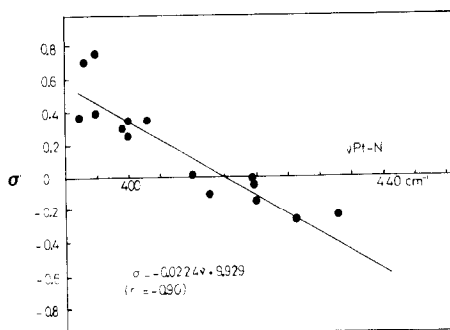
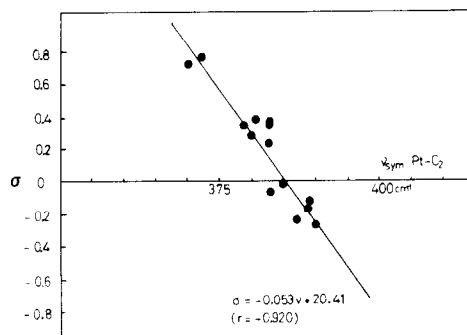
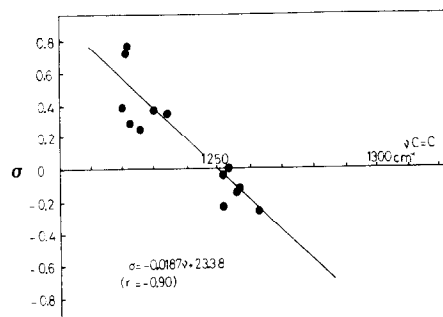
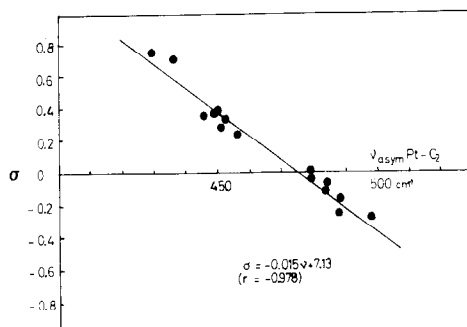
Fig. 1. Relationship between Hammett σ -value of R and $\nu\text{Pt}-\text{C}_2$.Fig. 2. Relationship between Hammett σ -value of R and $\nu\text{C}=\text{C}$ (upper diagram) and $\nu\text{Pt}-\text{N}$ (lower diagram).

TABLE 2

Infrared stretching frequencies for the complexes *trans*-[PtCl₂(CH₂=CH₂)(R-an)]

Substituent	σ	$\nu_{as}\text{Pt}-\text{C}_2$ (cm ⁻¹)	$\nu_s\text{Pt}-\text{C}_2$ (cm ⁻¹)	$\nu\text{C}-\text{C}$ (cm ⁻¹)	$\nu\text{Pt}-\text{N}$ (cm ⁻¹)
<i>p</i> -NO ₂	0.778	430	372	1222	394
<i>m</i> -NO ₂	0.710	437 ^a	370	1222	393
<i>m</i> -Br	0.391	450 ^a	381	1220	395
<i>m</i> -Cl	0.373	449 ^a	383	1230 ^a	403
<i>p</i> -I	0.352	446 ^a	379	1235 ^a	392
<i>p</i> -F	0.337	453	383	masked	400
<i>p</i> -I	0.276	451	380 ^a	1222	399
<i>p</i> -Br	0.232	456	383	1226	400
H	0	479	385	1255	410
<i>p</i> -OC ₆ H ₅	-0.028	480	384	masked	419
<i>m</i> -CH ₃	-0.069	484	383	1253	420
<i>p</i> -t-C ₄ H ₉	-0.120	483	389	1257	412
<i>p</i> -CH ₃	-0.170	488	389 ^a	1256 ^a	420
3,4-di-CH ₃	-0.240	487	387	1252	433
<i>p</i> -OCH ₃	-0.268	498	390	1263sh	426

^aMean of doublet.

and $\nu\text{C}-\text{C}$ (olefin). The assignments are readily made in relation to our earlier isotopic labelling study [1].

A plot of the frequencies of these four bands against σ is shown in Figs. 1 and 2 and the frequency data are presented in Table 2. It is clear that all of these bands move to higher frequency with electron releasing substituents, indicating that the electronic effects of the substituents are transmitted throughout the complex molecule. Electron withdrawing substituents have the opposite effect. It is interesting to note that the mass effects of the substituents do not appear to influence the frequencies to any marked extent.

The complexes discussed here differ from their substituted pyridine analogues [7] in that the latter fail to yield any correlation between $\nu\text{Pt}-\text{C}_2$ and σ . In fact, these bands remain approximately constant as R is varied in the pyridine series. This is probably associated with the fact that metal—ligand π -bonding is possible in the pyridine complexes but not in those of aniline.

Electronic spectra

The UV data are listed in Table 3. By analogy with similar complexes previously studied [8, 9] we expect to observe the $\pi \rightarrow \pi^*$ transitions of both the coordinated aniline and ethylene as well as the $5d \rightarrow \pi^*$ (ethylene) inverse charge transfer and the $\text{Cl}^- \rightarrow \text{Pt}^{2+}$ charge transfer bands. Although, because of the breadth of the electronic bands, no linear correlation exists, the maximum effect of R is on the $\pi \rightarrow \pi^*$ (aniline) transition as might be

TABLE 3

UV data for the complexes *trans*-[PtCl₂(CH=CH₂)(R·an)]

R	σ	λ_{\max} (nm)	ϵ	Assignment
<i>p</i> -NO ₂	0.778	240	8507	Cl ⁻ → Pt ²⁺
		288	9318	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		345	11546	$5d(\text{Pt}) \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{NO}_2)$ (or $n \rightarrow \pi^*(\text{NO}_2)$)
<i>m</i> -NO ₂	0.710	250	10442	Cl ⁻ → Pt ²⁺ , $\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		292	2520	$5d(\text{Pt}) \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{NO}_2)$
<i>m</i> -Br	0.391	241	7626	Cl ⁻ → Pt ²⁺ , $\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		299	1679	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>m</i> -Cl	0.373	249	6324	Cl ⁻ → Pt ²⁺ , $\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		300	1713	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>m</i> -I	0.352	241	11274	Cl ⁻ → Pt ²⁺
		~255	7333	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		299	1832	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>m</i> -F	0.337	248	5198	Cl ⁻ → Pt ²⁺
		~264	4709	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		296	1502	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -I	0.276	247	5648	Cl ⁻ → Pt ²⁺
		261	6764	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		302	1397	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -Br	0.232	252	9746	Cl ⁻ → Pt ²⁺ , $\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		301	2119	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
H	0	254	6301	Cl ⁻ → Pt ²⁺ , $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$, $\pi \rightarrow \pi^*(\text{an})$
		304	1613	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		~300	2898	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -PhO	-0.028	241	9758	Cl ⁻ → Pt ²⁺
		266	9310	$\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$, $\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{PhO})$
		~300	2898	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>m</i> -CH ₃	-0.069	248	6588	Cl ⁻ → Pt ²⁺
		257	6575	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		303	1948	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -t-C ₄ H ₉	-0.120	243	4768	Cl ⁻ → Pt ²⁺
		262	5585	$\pi \rightarrow \pi^*(\text{an})$, $\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$
		302	1568	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -CH ₃	-0.17	247	5334	Cl ⁻ → Pt ²⁺
		263	6818	$\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$, $\pi \rightarrow \pi^*(\text{an})$
		304	1885	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
3,4-di-CH ₃	-0.24	244	7696	Cl ⁻ → Pt ²⁺
		264	9252	$\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$, $\pi \rightarrow \pi^*(\text{an})$
		301	3026	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$
<i>p</i> -CH ₃ O	-0.268	241	4753	Cl ⁻ → Pt ²⁺
		273	8820	$\pi \rightarrow \pi^*(\text{C}_2\text{H}_4)$, $\pi \rightarrow \pi^*(\text{an})$
		325	1901	$5d(\text{Pt}) \rightarrow \pi^*(\text{C}_2\text{H}_4)$

expected. This is observed from the range of wavelengths which is spanned by the various transitions:

$\pi \rightarrow \pi^*(\text{aniline})$: 96 nm

$\pi \rightarrow \pi^*(\text{ethylene})$: 39 nm

$5d \rightarrow \pi^*(\text{ethylene})$: 33 nm

$\text{Cl}^- \rightarrow \text{Pt}^{2+}$: 8 nm

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