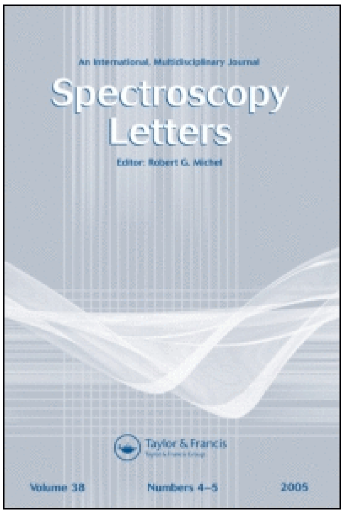

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Thomas P. E. Auf der Heyde[a]; Gary A. Foulds[a]; David A. Thornton[a]; Gareth M. Watkins[a]
[a] Department of Inorganic Chemistry, University of Cape Town, Rondebosch, South Africa

To cite this Article der Heyde, Thomas P. E. Auf , Foulds, Gary A. , Thornton, David A. and Watkins, Gareth M.(1981) 'The Infrared Spectra of Complexes of Variously-Substituted Anilines with Platinum (11) Halides', Spectroscopy Letters, 14: 6, 455 — 462

To link to this Article: DOI: 10.1080/00387018108062605

URL: http://dx.doi.org/10.1080/00387018108062605

SPECTROSCOPY LETTERS, 14(6), 455-462 (1981)

THE INFRARED SPECTRA OF COMPLEXES OF VARIOUSLY-SUBSTITUTED ANILINES WITH PLATINUM(II) HALIDES

Thomas P.E. Auf der Heyde, Gary A. Foulds,
David A. Thornton and Gareth M. Watkins
Department of Inorganic Chemistry,
University of Cape Town, Rondebosch 7700, South Africa

ABSTRACT

^{15}N- and d_5-labelling of the complexes *cis*- and *trans*-[Pt(aniline)$_2$Cl$_2$] and *cis*-[Pt(aniline)$_2$Br$_2$] has yielded firm assignments for the νPt-N and νPt-X bands in their far-infrared spectra. The far-infrared spectra of twenty-six complexes of general formula *cis*-[Pt(R-an)$_2$X$_2$] (R-an = variously-substituted anilines, X = Cl, Br) and *trans*-[Pt(R-an)$_2$Cl$_2$] have been determined. Comparison of their spectra with those of the parent aniline complexes yields assignments of νPt-N and νPt-X for each member of the series. The nature of the dependence of νPt-N and νPt-X on the Hammett σ-values of the substituents is discussed in relation to the potential anti-tumour activity of the complexes.

INTRODUCTION

cis-Amine complexes of platinum(II) halides have been widely investigated as potential anti-tumour agents[1]. Their anti-tumour properties depend, *inter alia*, on the steric, electronic and solubility effects of the coordinated amines. One way in which their electronic effects and hence their anti-tumour properties may be influenced is by the introduction of electron-withdrawing or electron-releasing substituents into the aniline ring. Since the metal-ligand stretching frequencies provide an index of the bond strengths, we have determined the far-infrared spectra of a wide range of the complexes $[Pt(R\text{-}an)_2X_2]$ (R-an = substituted aniline, X = Cl, Br) with the aim of eventually determining the nature of the correlation between the metal-ligand frequencies and anti-tumour properties.

EXPERIMENTAL

The *cis*-chloro complexes were prepared by adding an aqueous solution of $K_2[PtCl_4]$ (0.25g, 0.60 mmol) to an ethanolic solution of the aniline (2.40 mmol). After stirring for 16 hours the precipitated complex was collected by filtration and washed successively with water, ethanol and acetone (2 ml). The products were dried over silica gel. The *cis*- bromo complexes were similarly synthesized from an aqueous solution of $K_2[PtBr_4]$ prepared by allowing an aqueous solution of $K_2[PtCl_4]$ (0.25 g, 0.60 mmol) and an excess of KBr (2.28 g, 19 mmol) to stand for

30 minutes. The *trans*-complexes were prepared by dissolving the *cis*-isomer (synthesized from $K_2[PtCl_4]$ (0.30 g, 0.72 mmol)) and an excess of substituted aniline (2.90 mmol) in the minimum volume of *N,N*-dimethylformamide. The solution was heated under reflux (10 min.), cooled to room temperature and conc. HCl (2 ml) added. This solution was added to *M* NaCl (75 ml). The precipitate was collected by filtration, washed successively with water and ethanol and dried under reduced pressure over silica gel. Labelled complexes were similarly prepared from aniline-d_5 of 99% isotopic purity supplied by Merck, Sharp and Dohme (Canada) Ltd. and aniline-^{15}N of 97% isotopic purity supplied by BOC Prochem Ltd. Composition and purity of all compounds were determined by microanalysis (C,H,N).

Infrared spectra were determined on nujol mulls between CsI plates on a Beckman IR-12 spectrophotometer (500-300 cm^{-1}) and on nujol mulls between polyethylene plates on a Perkin-Elmer 180 spectrophotometer (400-150 cm^{-1}) and a Digilab FTS 16B/D interferometer (400-90 cm^{-1}).

RESULTS AND DISCUSSION

Although only the *cis*-complexes have potential anti-tumour activity, the infrared spectra of *trans*-$[Pt(R\text{-}an)_2Cl_2]$ along with those of *cis*-$[Pt(R\text{-}an)_2Cl_2]$ and *cis*-$[Pt(R\text{-}an)_2Br_2]$ will be discussed here. The far-infrared spectra of the complexes of the parent base (R = H) are reported in Table I which also lists

TABLE I

Far infrared frequencies and shifts induced by aniline labelling for the complexes [Pt(aniline)$_2$X$_2$] (cm^{-1})

X = Cl	Δν ^{15}N	Δν d_5	X = Br	Δν d_5	Assignment
cis-[Pt(aniline)$_2$X$_2$]					
451	5	41	446	39	NH$_2$ rock
374	4	11	367	12	νPt-N
330^a	0	0	223	0	νPt-X
293	2	10	290^a	10	νPt-N
220^a	0	12	236^a	7	γ ring
177	2	5	171	5	δN-Pt-N
147	0	3	141	1	δN-Pt-X
109	–^{b}	–^{b}	107	0	δX-Pt-X
trans-[Pt(aniline)$_2$Cl$_2$]					
449	5	38			NH$_2$ rock
374	4	12			νPt-N
340	0	0			νPt-Cl
222	0	13			γ ring
177	0	5			δN-Pt-N
142	0	2			δN-Pt-X
121	0	0			δX-Pt-X

[a] Mean of split peak. [b] Too broad for shift to be determined.

the shifts which these bands undergo on ^{15}N-labelling and d_5-deuteration of aniline. The assignments which result from the labelling work will be reported in detail elsewhere[2] but it is clear from Table I that νPt-N is firmly assigned to the bands within the range 360-375 and 290-300 cm^{-1} in the *cis*-complexes with only the higher frequency band being present in the *trans*-

complex. νPt-X is assigned to the only band within the range 200-350 cm^{-1} which is unaffected by both ^{15}N- and d_5-labelling.

In the spectra of the complexes of the variously-substituted anilines (Fig. 1), only the strong higher-frequency component of the two νPt-N bands will be used to probe the substituent effects. Using the firm assignments of νPt-N and νPt-X in the complex with R = H as a basis, comparison with the spectra of the complexes with other substituents clearly shows which bands in their spectra have the corresponding assignments. The frequencies are reported in Table 2.

The infrared data show that the effect of electron-withdrawing substituents (positive σ) is to increase νPt-N while νPt-Cl remains relatively unaffected. This indicates a withdrawal of electron density from the Pt(II) ion without changing the electron density in the Pt-X bonds. This effect has also been noted[3] in the *trans*-[Pt(C_2H_4)(4-R-py)Cl_2] complexes (where R-py represents a range of variously-substituted pyridines) in which only νPt-N was found to exhibit a dependence on R. In the series of substituted pyridine complexes, no regular relationship between νPt-N and σ was observed. This was considered to be due to the opposing influences of a particular substituent on the σ- and π-bonding between the platinum(II) ion and the pyridine ring. In the aniline series, no π-bonding is possible and the substituent influences only the σ-bonding between Pt(II) and the

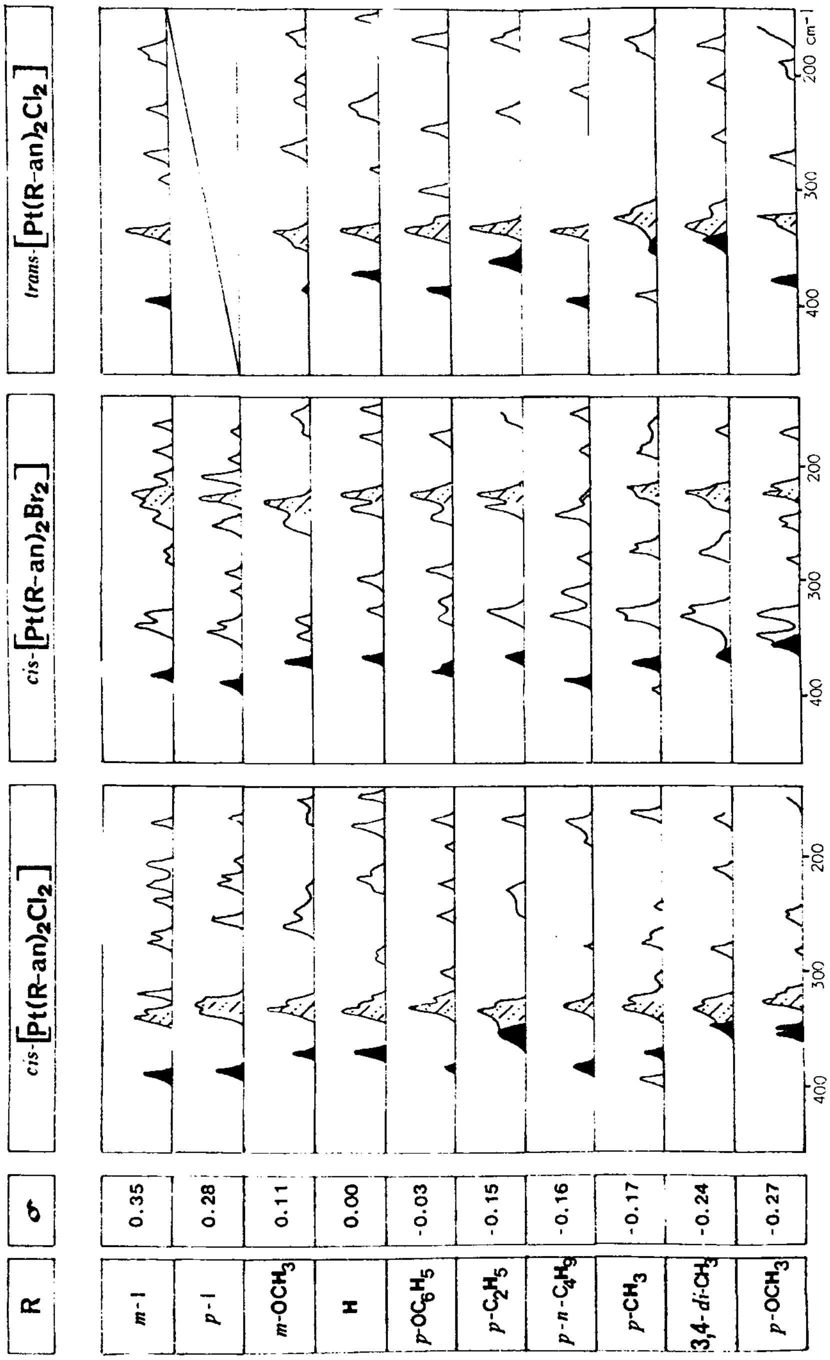

FIGURE 1: Assignment of ν(Pt-N) (solid bands) and ν(Pt-X) (shaded bands) for the series $[Pt(R\text{-}an)_2X_2]$

TABLE 2

νPt-N and νPt-X frequencies for complexes [Pt(R-an)$_2$X$_2$]

R	σ	*cis*- [Pt(R-an)$_2$Cl$_2$]		*cis*- [Pt(R-an)$_2$Br$_2$]		*trans*- [Pt(R-an)$_2$Cl$_2$]	
		νPt-N	νPt-Cl[a]	νPt-N	νPt-Br[a]	νPt-N	νPt-Cl
m-I	+0.35	390	341	381	222	396	335
p-I	+0.28	387	331	390	225		
m-OCH$_3$	+0.11	372	336	367	231	381	335
H	0	371	338	366	223	372	338
p-OC$_6$H$_5$	-0.03	384	336	380	223	384	335
p-C$_2$H$_5$	-0.15	360	335	365	225	359	334
p-n-C$_4$H$_9$	-0.16	383	330	388	226	394	335
p-CH$_3$	-0.17	373	333	372	219	350	321
3,4-di-CH$_3$	-0.24	355	334	365	224	352	333
p-OCH$_3$	-0.27	356[a]	329	352[a]	225	378	329

[a] Split peaks

amine. In this case, a regular correlation is observed.

The nature of the effect of the substituents on the antitumour properties of the *cis*-complexes must await the results of animal studies. From the results of the infrared spectra, the most likely effect is that the lipid-solubility of the complexes will be reduced by electron-withdrawing substituents which apparently remove electron density from the Pt(II) ion and thus increase the ionic character of the Pt-N bond. From this point of view, electron-releasing substituents should favour the antitumour activity.

ACKNOWLEDGEMENTS

We thank the University of Cape Town Research Committee and the South African Council for Scientific and Industrial Research for financial assistance.

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Received: April 30, 1981
Accepted: May 15, 1981