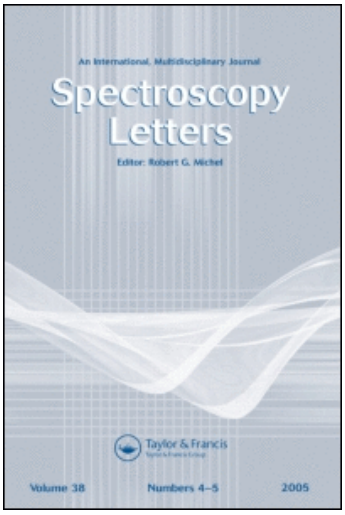


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

IR- and UV-Spectral Study on the Mechanism of 2-Aminopyridine Complexation with Palladium (II)

Sh. Dinkov[a]; M. Arnaudov[a]
[a] Department of Chemistry, University of Sofia, Sofia, Bulgaria

To cite this Article Dinkov, Sh. and Arnaudov, M.(1998) 'IR- and UV-Spectral Study on the Mechanism of 2-Aminopyridine Complexation with Palladium (II)', Spectroscopy Letters, 31: 3, 529 — 546
To link to this Article: DOI: 10.1080/00387019808002747
URL: http://dx.doi.org/10.1080/00387019808002747

SPECTROSCOPY LETTERS, 31(3), 529-546 (1998)

IR- AND UV-SPECTRAL STUDY ON THE MECHANISM OF 2-AMINOPYRIDINE COMPLEXATION WITH PALLADIUM (II)

Key words: IR- and UV-spectra; 2-Aminopyridine; Pd (II)-Complexes

Sh. Dinkov and M. Arnaudov*

University of Sofia, Department of Chemistry
1, J. Bourchier Blvd., 1126 Sofia, Bulgaria

ABSTRACT

The IR-spectra of Pd (II) complexes with 2-aminopyridine, obtained both in sulphuric acid and alkaline solution are studied in the region 1700-1400 cm^{-1}. The structural conclusions are based on comparison with the IR- and UV-spectra of the free ligand and aminopyridinium sulphate, as well as of trans-dichloro-di-2-aminopyridine-palladium and deuterated at the amino group analogues of the investigated compounds.

* Corresponding author

INTRODUCTION

In a recent paper [1] we have described the data received in our IR- and UV-spectral investigation on Pd (II) complexes with 2-aminopyridine (*2-AP*). It was found that when obtained in sulphuric acid medium sulphato-2-aminopyridine-palladium complex (*SAPPD*) has a polynuclear structure as a result of the bridging co-ordination of both the sulphato group and *2-AP*. Due to bidentate co-ordination of the organic ligand, the complex keeps its oligomeric structure in alkaline solution, in which the substitution of SO_4^{2-} by OH^- yields the hydroxo-2-aminopyridine-palladium complex (*HAPPD*).

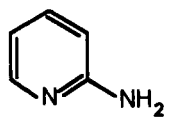
As a rule *2-AP* is a monodentate ligand, since the endocyclic nitrogen exhibits significantly stronger electron-donating power than the amino group [2]. Because of that, its bidentate co-ordination in *SAPPD* and *HAPPD* is proved on the ground of a series of comparative studies. The present study is based on the following previous results:

- The NH_2 stretching region in the *SAPPD* and *HAPPD* spectra is completely different compared to those of the free ligand and trans-dichloro-di-2-aminopyridine palladium (*trans*-$[Pd(2\text{-}AP)_2Cl_2]$). The latter complex exhibits a monodentate co-ordination of *2-AP* via the pyridine nitrogen atom [3]. The well defined free ligand bands (0.0001 M solution in carbon tetrachloride), corresponding to antisymmetric ($\nu_{as}(NH_2)$) and symmetric ($\nu_s(NH_2)$) stretching frequencies at 3510 cm^{-1} and 3408 cm^{-1} respectively, are only low-frequency shifted by the $Pd^{2+} \leftarrow$ N(Py) dative bond formation in the chloro complex ($\nu_{as}(NH_2)$ = 3444 cm^{-1}, $\nu_s(NH_2)$ = 3346 cm^{-1}). As a result of the *2-AP* bidentate co-ordination, *SAPPD* and *HAPPD* spectra show wide overlapping bands between 3500 cm^{-1} and 3100 cm^{-1} which are difficult for NH_2 stretching bands identification.

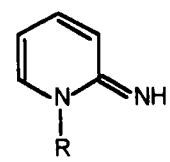
- The UV-spectral data correspond to the above suggestions. The spectra of *2-AP* and *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ exhibit *p*- and α-bands at 230 nm and 290 nm, typical of the pyridine aromatic structure (**I**). However, the bands at 230 nm and 290 nm are not observed in *SAPPD* and *HAPPD* spectra, where a new absorption maximum appears at 255 nm. Two possible explanations of this phenomenon suggest the bidentate co-ordination of *2-AP* as follows:

- The blocking of the free electron pair of exocyclic *2-AP* nitrogen vanishing the electron donor effect of the amino group causes a hypsochromic shift of the *p*-band and makes the α-absorption maximum the only band about 250 nm.

- The band about 255 nm is characteristic of the pyridone-imine structure (**II**), which is observed in 1-methyl-2-pyridone-imine (R = CH_3)[4]. The possibility for the stabilization of pyridone-imine form of *2-AP* (R = H) in both the sulphato and hydroxo complexes could also be considered as the consequence of the electron density redistribution by an additional $Pd^{2+} \leftarrow$ N(amino) dative bond formation.



(I)



(II)

In order to confirm the conclusions stated above, the present paper deals with the 1700-1400 cm^{-1} IR-spectra of the discussed complexes, of the free ligand and 2-aminopyridinium sulphate, as well as of their amino group deuterated derivatives. The presence of a bidentate co-ordination

with partially expressed pyridone-imine structure of the organic ligand in *SAPPD* and *HAPPD* is additionally proved by comparison with the appropriate UV-spectral analysis.

EXPERIMENTAL

2-AP (Fluka, purum) recrystallized from n-hexane was used. *SAPPD*, *HAPPD* and *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ were synthesized as previously described [1, 3].

2-Aminopyridinium sulphate was prepared by dissolution of 1.88 g (0.02 mol) *2-AP* in 10 ml 1M H_2SO_4 (0.01 mol) followed by vacuum evaporation of the solution to dryness. Deuterated compounds were obtained by synthesis in D_2O. The isotopic exchange was monitored through the disappearance of the NH_2 stretching absorption.

The IR-spectra were recorded on a Bruker Vector 22 FTIR-spectrometer. The solid state spectra were taken as Nujol mulls. The technics in pells was non-applicable since the complexes decompose upon pressing in KBr. The spectrum of *2-AP* (0.1 M) in dimethyl sulphoxide (*DMSO*) and those of the saturated D_2O solutions were obtained by using CaF_2-cells with 0.007 cm and 0.002 cm path length, respectively.

The UV-spectra were measured with a Specord UV-VIS spectrometer at 0.0001 M concentration and 0.5 cm path length.

RESULTS and DISCUSSION

The IR-spectra (1700-1400 cm^{-1}) of the investigated compounds and their deuterated analogues are given in Figs. 1-3 and 6, the wavenumbers of the corresponding absorption maxima are summarized in Table 1. The *2-AP* spectrum is obtained in *DMSO* (Fig. 1.1). In this solvent we take into

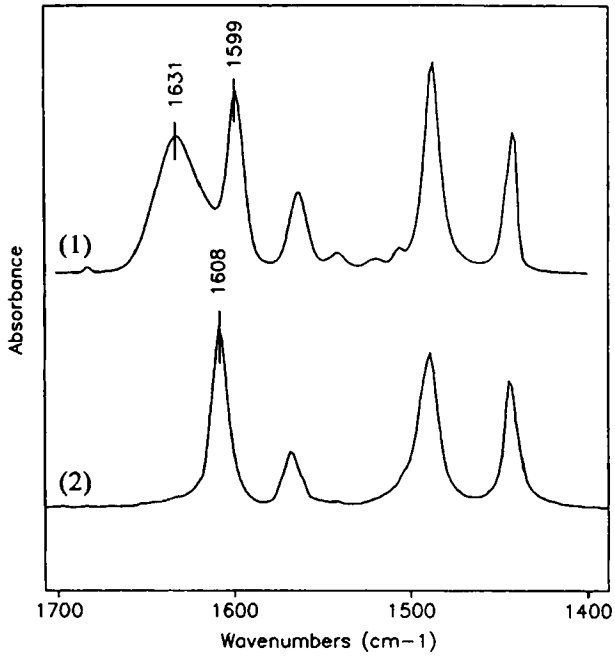


Fig. 1. IR-spectra of *2-AP* solution in: *DMSO* (1); D_2O (2)

consideration the effect of NH...O=S hydrogen bond formation, which is possible with *SAPPD*.

The following experimental data confirm our previous conclusions [1]:

- a very good correspondence between the spectral curves of *SAPPD* and *HAPPD* (Figs. 2.1 and 2.4) proving the identical mode of co-ordination of *2-AP* in both complexes;

- coincidence of *SAPPD* spectrum in D_2O with that of the product, isolated from heavy water (see Figs. 2.2 and 2.3) suggesting structure identity both in solution and in the solid state.

The isotopic exchange eliminates the NH_2 bending bands ($\delta(NH_2)$) and provides a possibility to find the effect of co-ordination on the pyridine

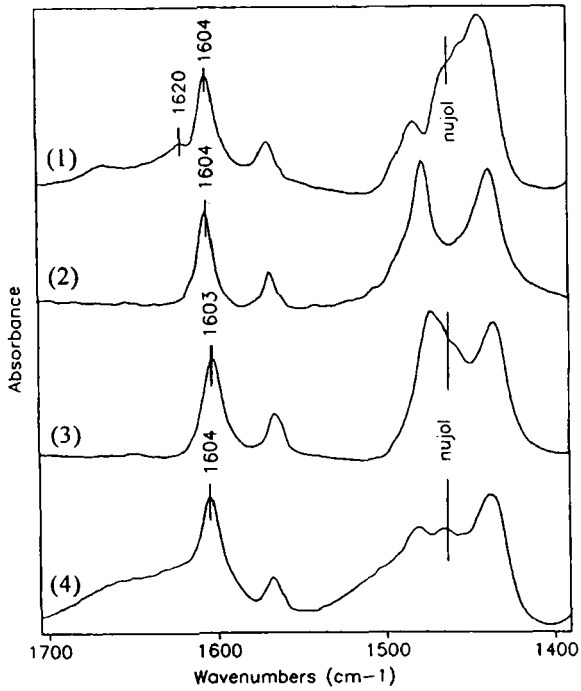


Fig. 2. IR-spectra of: *SAPPD* - Nujol mull (**1**), solution in D_2O (**2**); deuterated *SAPPD*, Nujol mull (**3**); *HAPPD*, Nujol mull (**4**)

ring frequencies by studying the spectra of deuterated products. Amino group deuterated *2-AP* exhibits absorption bands at 1608 cm^{-1}, 1568 cm^{-1}, 1489 cm^{-1} and 1444 cm^{-1} (Table 1 and Fig. 1.2). It is proved [5] that the first one is the most sensitive to the electronic effects of the substituents in the pyridine ring. In particular, upon strong electron acceptor influence on the endocyclic nitrogen as in pyridine N-oxides, the corresponding absorption maximum is shifted up to 1630-1620 cm^{-1}. Exactly the same high-frequency shift is observed in the spectra of *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ and its deuterated analogue (Table 1 and Fig. 3), where the

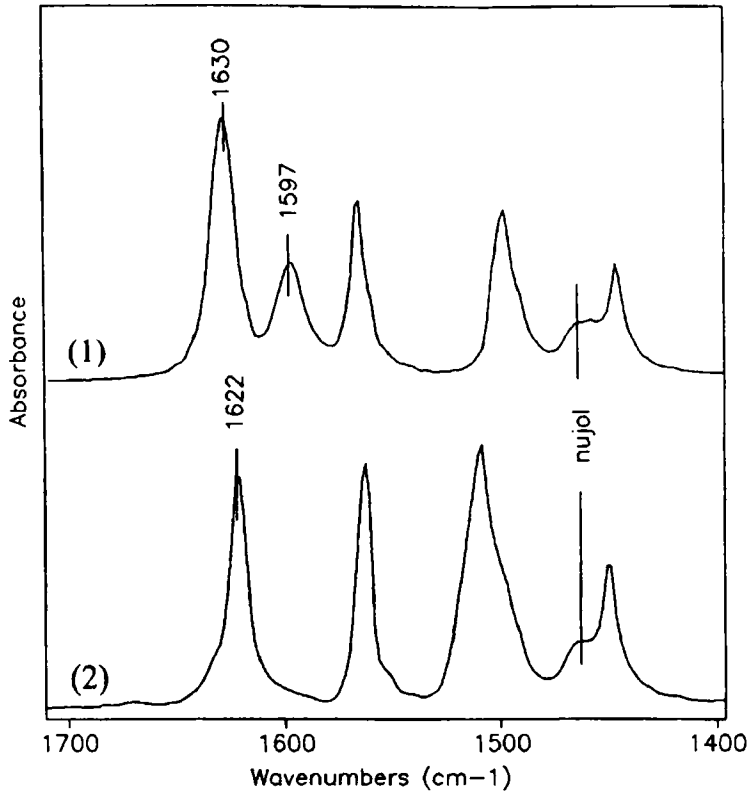


Fig. 3. IR-spectra (Nujol mulls) of: *trans*-[*Pd(2-AP)*$_2$*Cl*$_2$] (**1**); the deuterated complex (**2**)

electron acceptor effect is realized through the dative Pd $^{2+}\leftarrow$ N(Py) interaction. The frequency of the discussed band is decreased to 1604-1603 cm^{-1} in deuterated *SAPPD* spectra (Figs. 2.2 and 2.3). A similar "opposite effect" is found for pyridine N-oxides in the presence of electron acceptor substituents in α-position [5]. The comparison of these data is an additional proof for the bidentate co-ordination of *2-AP* in *SAPPD* and *HAPPD*, since the formation of a supplementary Pd $^{2+}\leftarrow$ N(amino) dative

TABLE 1

IR-spectral data (cm^{-1}) of the investigated compounds in the 1700-1400 cm^{-1} range

Compound	Assignment				
	δ(NH)+δ(HOH)	*ring frequencies*			
2-AP					
solution in *DMSO*	1631	1599	1562	1487	1442
solution in D_2O		1608	1568	1489	1444
SAPPD					
Nujol	1670-1615	1604	1568	1481	1442
deuterated, in D_2O		1604	1568	1477	1437
deuterated, Nujol		1603	1566	1473	1435
HAPPD					
Nujol	1670-1615	1604	1568	1479	1439
trans-[Pd(2-AP)$_2$Cl$_2$]					
Nujol	1597	1630	1566	1498	1446
deuterated, Nujol		1622	1562	1508	1450
2-Aminopyridinium sulphate					
Nujol	1666, 1645$^{(sh)}$*,1628				1488
deuterated, Nujol	1646*	1588, 1532			

*ν(C=N) - possible assignment

bond converts the amino group into an effective electron acceptor substituent.

The isotopic exchange at *SAPPD* eliminates the series of low-intensity absorption bands between 1670 cm^{-1} and 1615 cm^{-1}, which are also observed in *HAPPD* spectrum (Table 1 and Fig. 2). These bands correspond to NH bending frequencies, as well as to *δ(HOH)* of water which might be included in the complexes. Curve fitting of *SAPPD* and *HAPPD* spectra in this range specifies the following results (Figs. 4 and 5).

The complete coincidence of the resolved bands of both complexes once again indicates their identical structure. The 1642-1641 cm^{-1} absorption maxima in both spectra could be attributed to *δ(HOH)* of water molecules co-ordinated to the terminal Pd^{2+} ions. For reasons stated below, we assign to the $\delta(NH_2)$ frequency in *SAPPD* and *HAPPD* the bands at 1620 cm^{-1} and 1618 cm^{-1}, respectively (see also Fig 2.1). On the ground of literature data [6-12], the corresponding value of the free ligand varies from 1635 cm^{-1} to 1613 cm^{-1}. These data coincide with our results on IR-spectra of *2-AP*, measured at various solute concentrations in ten solvents with different solvating ability, including strong organic bases like triethylamine [13]. This small $\Delta\delta(NH_2)$ interval suggests that $\delta(NH_2)$ frequency of *2-AP* is low-sensitive to the association effects. For this reason, the obtained from *SAPPD* spectrum value of 1620 cm^{-1} (Fig. 4), coincides with $\delta(NH_2)$ in *2-AP* spectrum, recorded at 0.05 M solute concentration in carbon tetrachloride [7] and is 10 cm^{-1} lower than that of the free ligand in *DMSO* (Fig. 1.1 and Ref. [8]). On the other hand, the NH_2 stretching bands in *SAPPD* spectrum [1] are low-frequency shifted below 3200 cm^{-1} indicating the presence of NH...O=S hydrogen bonds. This assumption is confirmed by IR-spectral study of sulphato-di-aniline palladium (II) [13]. The above

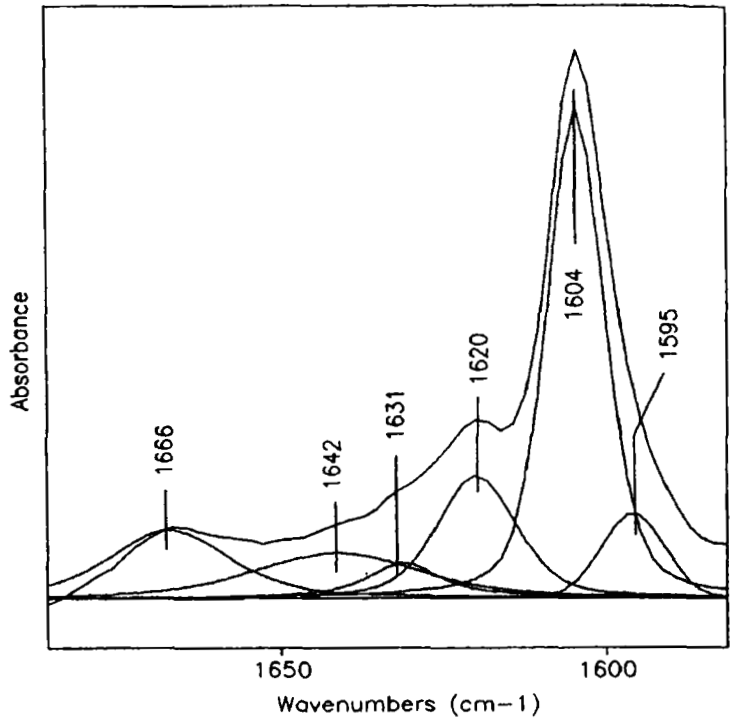


Fig. 4. Curve fitting (1700-1550 cm^{-1}) of *SAPPD* spectrum, Nujol mull

discussion applies to the effects of NH...O(H) hydrogen bond formation on *HAPPD* spectrum too (Fig. 5). However, the isotopic exchange data show that $\delta(NH_2)$ value is lowered to 1597 cm^{-1} in *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ (Fig. 3), which is an additional indication about the different way of complexation between Pd^{2+} and *2-AP* in chloride complex compared to *SAPPD* and *HAPPD*, respectively.

The main result obtained by the IR-spectral analysis is the presence of the 1666-1665 cm^{-1} and 1631-1630 cm^{-1} absorption maxima in *SAPPD* and *HAPPD* IR-spectra (Figs. 4 and 5). These bands are typical of 2-amino-

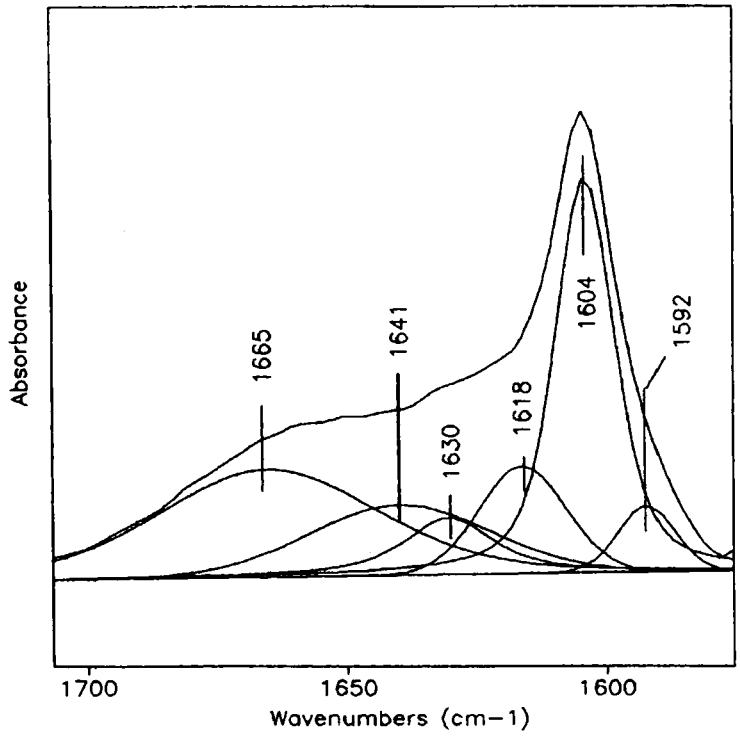


Fig. 5. Curve fitting (1700-1550 cm^{-1}) of *HAPPD* spectrum, Nujol mull

pyridinium chloride and according to Ref. [14] they assign the δ $(=N^{+}H_2)$ modes of the pyridone-imine structure (**IV**). Our study on 2-amino-pyridinium sulphate confirms this assumption. The corresponding IR-spectrum exhibits strongly expressed absorption maxima at 1666 cm^{-1} and 1628 cm^{-1} (Fig. 6.1) which disappear after deuteration (Fig. 6.2). On the other hand, the absence of the bands at about 1600 cm^{-1} and 1565 cm^{-1}, typical of the *2-AP* pyridine ring (Table 1, compare Figs.1 and 2 with 6), gives an experimental evidence about a shift of the prototropic equilibrium of 2-aminopyridinium sulphate and generally of *2-AP* monocations (see

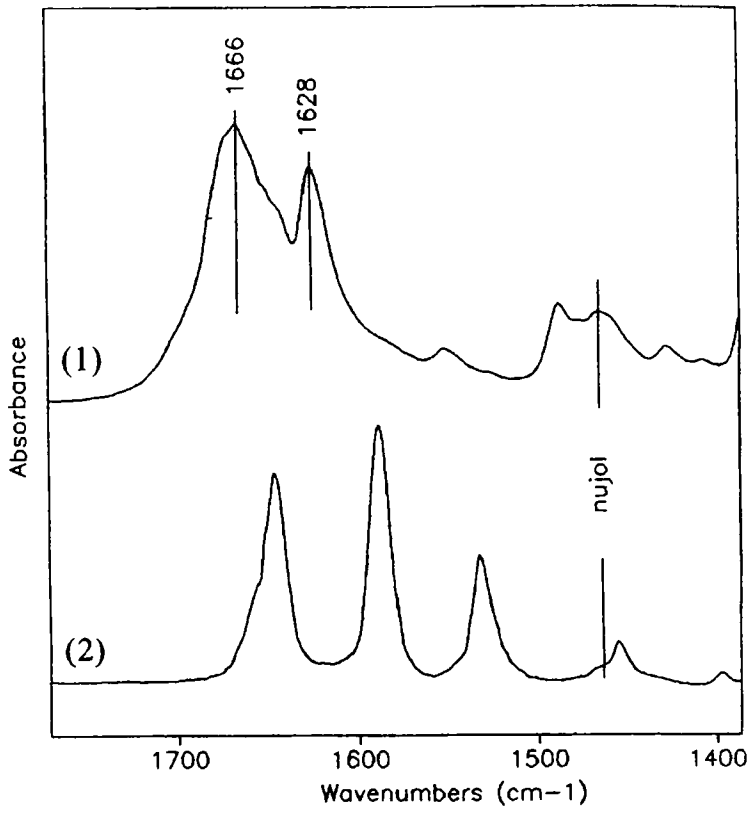
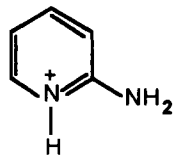


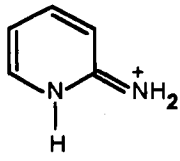
Fig. 6. IR-spectra (Nujol mulls) of: 2-Aminopyridinium sulphate (**1**); the deuterated compound (**2**)

Ref. [14]) to the pyridone-imine form (**IV**). Since the positive charge in them is localized mainly at the exocyclic nitrogen, this structure could be considered as an extreme analogue of the co-ordinated through NH_2 group *2-AP*, where the dative bond formation also creates a partial positive charge at the exocyclic nitrogen. Therefore, the appearance of the additional bands at 1666-1665 cm^{-1} and 1631-1630 cm^{-1} in the IR-spectra of *SAPPD* and *HAPPD* can be considered as a direct proof about a partial

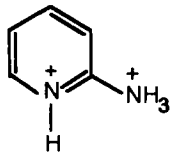
stabilization of the pyridone-imine structure in both complexes. Since the discussed bands are absent in the IR-spectrum of *trans*-[*Pd(2-AP)*$_2$*Cl*$_2$] (Fig. 3.1), it is regular to suggest that the difference is due to the formation of a $Pd^{2+}\leftarrow$ N(amino) dative bond in *SAPPD* and *HAPPD*.



(III)



(IV)



(V)

The IR-data discussed above are in the following correspondence with the results of the UV-spectral analysis:

The UV-spectra of 0.0001 M aqueous solution of *SAPPD* and *HAPPD* (Figs. 7.1 and 7.2) exhibit well defined absorption maximum at 255 nm (ε = 6200 $mmol^{-1}.cm^2$ and 5200 $mmol^{-1}.cm^2$, respectively). As discussed above, the origin of this band could be explained in terms of: (i) blocking of the free electron pair of N(amino) nitrogen of *2-AP*, caused by $Pd^{2+}\leftarrow$ N(amino) bond formation ; (ii) stabilization of pyridone-imine form.

These effects appear as a result of a bidentate coordination of the organic ligand in both complexes (see structure **VI** and **VII**) and the IR-spectral data suggest thier co-existence. The UV-spectral analysis of 2-aminopyridinium salts prove the presence of the first one.

The UV-spectrum (Fig. 7.3) of 2-aminopyridinium sulphate (solution of *2-AP* in 10% H_2SO_4) exhibits two absorption maxima at 230 nm (ε = 9100 $mmol^{-1}.cm^2$) and 303 nm (ε = 6400 $mmol^{-1}.cm^2$), respectively. This result corresponds to previously published data about *2-AP* solutions in 1% and

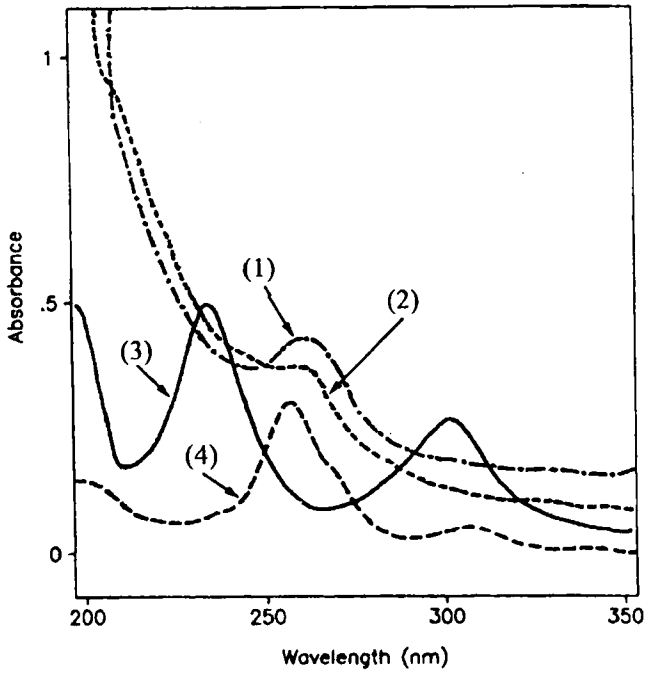
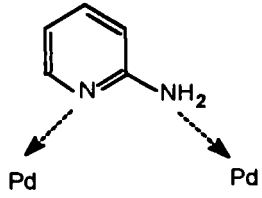


Fig. 7. UV-spectra of: *SAPPD* (**1**) and *HAPPD* (**2**), solution in H_2O; *2-AP*, solution in: 10% H_2SO_4 (**3**) and 96% H_2SO_4 (**4**)

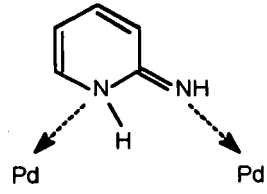
66% H_2SO_4 [2]. We have obtained the same spectrum in the case of 2-aminopyridinium chloride with λ_{max} = 232 nm (ε = 9000 $mmol^{-1}.cm^2$) and 303 nm (ε = 6200 $mmol^{-1}.cm^2$). These absorption maxima are very close to *p*- and α-bands at 230 nm (ε = 9570 $mmol^{-1}.cm^2$) and 288 nm (ε = 4080 $mmol^{-1}.cm^2$) respectively, in the UV-spectrum of *2-AP* (aqueous solution) [2]. This analogy suggests an aromatic structure (**III**) of the stabilized in solution *2-AP* monocations, i.e. the pyridone-imine structure (**IV**), which is discussed in Ref. [14] and confirmed in our IR-study, is characteristic only of the solid state samples.

Further UV-spectral study of *2-AP* in 96% H_2SO_4 (Fig. 7.4), shows the presence of only one absorption maximum at 258 nm (ε = 5600 $mmol^{-1}.cm^2$). This result is very close to the analogous data for N-methyl and N,N-dimethylaminopyridine in 98% H_2SO_4 (λ_{max} = 257 nm, ε = 6600 $mmol^{-1}.cm^2$ and 6460 $mmol^{-1}.cm^2$, respectively) [2]. Since N,N-dimethyl-2-aminopyridine does not exhibit prototropic isomerisation, it is evident that the discussed band does not indicate the appearance of a pyridone-imine form. Therefore, in concentrated H_2SO_4 *2-AP* gives the dication (**V**), where the free electron pairs of both nitrogen are blocked. This vanishes the n→π conjugation between the amino group and the pyridine ring and causes a strong hypsochromic shift of the *p*-spectral band. The same effect was observed by comparing the UV-spectra of aniline and its cation in H_2SO_4 solution [15].

The formation of the bidentate structure (**VI**) in *SAPPD* and *HAPPD* should also block the free electron pairs of both nitrogen in *2-AP* vanishing the electron donor effect of the amino group. The complete analogy with *2-AP* dication structure (**V**) explains the similarity of their UV-spectra (compare Figs. 7.1 and 7.2 with 7.4).



(**VI**)



(**VII**)

In summary, both the IR and UV spectral results confirm our suggestion about a bidentate co-ordination of *2-AP* yielding an oligomeric structure of

SAPPD and *HAPPD* [1]. However, the UV-spectral analysis can not prove whether the complexation in solution is realized according to scheme (**VI**) and /or (**VII**), since both structures are characterized by a 255 nm band. The IR-spectral results in the solid state prove the partially expressed pyridone-imine structure of *2-AP* in both complexes. On the other hand, the analysis of the IR-spectra in heavy water suggests the equality of *SAPPD* and *HAPPD* structure both in solution and in the solid state. Therefore, we can accept that the bidentate co-ordination of the organic ligand proceeds in two parallel schemes (**VI** and **VII**) with the priority of structure (**VI**). According to quantum chemical calculations [16] , the exocyclic nitrogen atom in *2-AP* imino form (**II**, R = H) exhibits higher electron density compared to the pyridine nitrogen. Therefore, the pyridone-imine structure should be stabilized at the outlying units of the polynuclear chains in *SAPPD* and *HAPPD*, where Pd^{2+} ions are bonded to *2-AP only* through a dative $Pd^{2+}\leftarrow$ N(amino) bond providing the stabilization of the polynuclear complex at a given length.

ACKNOWLEDGMENTS

The financial support from the National Foundation for Promotion of Science (Project No X-310) is gratefully acknowledged.

REFERENCES

1. Arnaudov M., Dinkov Sh., Shishkova L., Pindeva L., Petrov H. and Dobreva E. IR- and UV-spectral Investigation of Palladium (II) Complexes with 2-Aminopyridine Obtained in Sulphuric Acid and Alkaline Solutions. Spectrosc. Lett. (in press).
2. Dega-Szafran Z., Kania A., Nowak-Widra B. and Szafran M., UV, ^{1}H and ^{13}C NMR Spectra, and AM1 Studies of Protonation of Aminopyridines. J. Mol. Structure 1994; 322: 223.

3. Gomes-Vaamonde C., Alvares-Valdes A., del C. Navarro-Ranninger M. and Masaguer J.R., Synthesis and Characterization of Complexes of Pd (II) with 2-Aminopyridine. Trans. Met. Chem. 1984; 9: 52.

4. Mason S.F.,The Electronic Spectra of N-Heteroaromatic Systems. Part VI. The $\pi \rightarrow \pi$ Transition of Monocyclic Amino- and Mercapto-azines. J. Chem. Soc. 1960: 219.

5. in: Katritzky A.R. ed. *Physical Methods in Heterocyclic Chemistry.* New York and London: Academic Press 1963: Chap.10.

6. Angyal C.L. and Werner R.L. The Tautomerism of N-Heteroaromatic Amines. Part II. Infra-red Spectroscopic Evidence. J. Chem. Soc. 1952: 2911.

7. Ramiah K.V. and Puranik P.G., Infrared Spectroscopic Studies of the Association of Amino-pyridines. J. Mol. Spectrosc. 1961; 7: 89.

8. Thompson W.K. Infrared Absorption Spectra of Dimethyl Sulphoxide Solutions. Part I. Heterocyclic Amines. J. Chem. Soc. 1962: 617.

9. Yagudaev M.R. and Schejkner Yu.N. Integral'naya Intensivnost' Polos Deformatsionnyh Kolebanij Pervichnoj Amino-gruppy. Dokl. Akad. Nauk SSSR, ser. Fiz. Khim. 1962; 144: 177.

10. Yagudaev M.R., Popov E.M., Yakovlev I.P. and Schejkner Yu.N. Chastoty i Intensivnosti Infrakrasnyh Polos Poglostcheniya Valentnyh i Deformatsionnyh Kolebanij Gruppy NH_2 v Pervichnyh Aminah. Izv. Akad. Nauk SSSR, ser. Khim. 1664; 7: 1189.

11. Berezin V.I. and El'kin M.D. Kolebatel'nye Spektry i Geometricheskaya Struktura Anilina, α–,β–,γ–Aminopiridinov. Optika I spektrosk. 1974; 36: 905.

12. Carmona P., Molina M. and Escobar R. Studies on Aminopyridines in Aqueous Solution by Laser Raman Spectroscopy. Spectrochim. Acta 1993; 49A 1.

13. Arnaudov. M. and Dinkov Sh. Unpublished Results.

14. Spinner E. The Vibritional Spectra and Structures of the Hydrochlorides of Aminopyridines. J. Chem. Soc. 1962 : 3119.

15. DMS, UV-atlas of Organig Compounds, Vol. 4, Spectra No No D6/3 and D6/4, Verlag Chemie, Weinheim; Butterworths, London, 1968.

16. Konishi H., Kato H. and Yonezawa T. The Electronic Structure of Aminopyridines and their Mono- and Di-protonated Cations. Theoret. Chim. Acta (Berl.), 1970; 19: 71.

Date Received:September 3, 1997
Date Accepted: November 29,1997