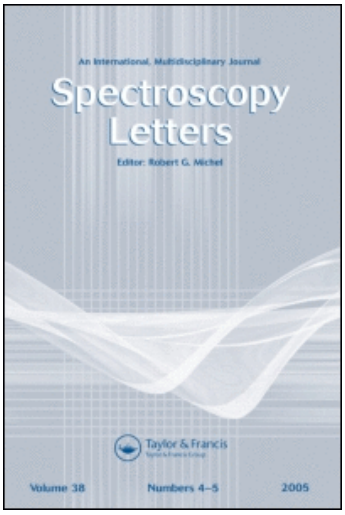

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Arnaudov, M. , Dinkov, Sh. , Shishkova, L. , Pindeva, L. , Petrov, C. and Dobreva, E.(1997) 'IR- and UV-Spectral Study of Palladium(II) Complexes with 2-Aminopyridine Obtained in Sulphuric Acid and Alkaline Solutions', Spectroscopy Letters, 30: 8, 1595 — 1607
To link to this Article: DOI: 10.1080/00387019708006746
URL: http://dx.doi.org/10.1080/00387019708006746

SPECTROSCOPY LETTERS, 30(8), 1595-1607 (1997)

IR- AND UV-SPECTRAL STUDY OF PALLADIUM (II) COMPLEXES WITH 2-AMINOPYRIDINE OBTAINED IN SULPHURIC ACID AND ALKALINE SOLUTIONS

Key words: 2-Aminopyridine, Pd (II) complexes, IR- and UV-spectra

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ABSTRACT

When obtained in sulphuric acid medium sulphato-2-aminopyridine-palladium (II) complex has a polynuclear structure, with a bridging co-ordination of both the sulphato-group and 2-aminopyridine. The complex keeps its polynuclear structure in alkaline solution, in which the substitution of sulphato ions by hydroxylic groups yields hydroxo-2-aminopyridine-palladium (II). The compounds discussed are the main

components of activators used in currentless metallization of non-conducting surfaces.

INTRODUCTION

The alkaline solutions of Pd (II) complexes with amino group containing ligands have been successfully utilized as activators in the currentless metallization of non-conducting surfaces. Our previous investigations on this problem [1, 2] show that best quality of the activator is achieved by consecutive dissolution of palladium sulphate and 2-aminopyridine (*2-AP*) in sulphuric acid followed by alkalization of the obtained solution. Sulphato-2-aminopyridine palladium complex (*SAPPD*), obtained at the first stage of this method, changes after the addition of base into hydroxo complex (*HAPPD*). This two-stage method is involved because when directly obtained in base medium the complex does not provide good technological quality of the activator.

In view of this, the purpose of the present paper is to characterize the composition and structure of palladium (II) complexes with 2-aminopyridine, obtained in sulphuric acid medium with a following alkalization. Although various complexes are known with the participation of *2-AP* [3-5], the compounds investigated in the present paper are not discussed before. Since direct X-ray analysis is impeded by the amorphous character of the isolated solid compounds, their structure is studied by comparison with IR- and UV-spectra of the free ligand and of trans-dichloro-di-2-amino-pyridine-palladium (*trans*-$[Pd(2\text{-}AP)_2Cl_2]$). The comparison with the latter compound is performed because of the

monodentate co-ordination of *2-AP* in this complex through the nitrogen atom of the pyridine ring [6].

EXPERIMENTAL

Materials

2-Aminopyridine (Fluka, purrum) recrystallized from n-hexane and *palladium sponge* (Herraeus, 99.95%) were used. The other reagents were Merck, p.a.

Synthesis

Palladium sulphate ($PdSO_4$) and *trans-dichloro-di-2-aminopyridine palladium* (*trans*-$[Pd(2\text{-}AP)_2Cl_2]$), were obtained according to the methods described elsewhere [6, 7].

Sulphato-2-aminopyridine-palladium complex (*SAPPD*):

2-AP (1.88 g, 0.02 mol) dissolved in 15 ml H_2SO_4 (4 M) is added to 15 ml solution of $PdSO_4$ (4.05 g, 0.02 mol) in H_2SO_4 (4 M). The mixture is kept for 10 hours at 20° C, then 120 ml of absolute methanol are added. The obtained yellow precipitate is filtrated, washed three times with methanol and dried at room temperature. The yellow colored powder substance is dissolved in water and then evaporated to dryness. The red product is amorphous. Analysis: see Table 1.

Hydroxo-2-aminopyridine-palladium complex (*HAPPD*):

$Ba(OH)_2$ is added to the solution of *SAPPD* (1 g in 100 ml H_2O) as far as the SO_4^{2-} ions are completely precipitated. The separated $BaSO_4$ is filtrated and the filtrate is evaporated to dryness at 50° C. The obtained red non-crystal substance is soluble both in sodium hydroxide and sulphuric acid. Analysis: see Table 1.

TABLE 1

Calculated and experimentally determined chemical composition of *SAPPD* and *HAPPD*

	wt %				
	Pd	C	H	N	SO_4^{2-}
	$[Pd_6(2\text{-}AP)_5(SO_4)_5](OH)_2.2H_2O$				
calculated	38.50	18.09	2.17	8.44	28.94
experimental	38.50	17.93	2.85	8.05	29.03
	$[Pd_6(2\text{-}AP)_5(OH)_{10}](OH)_2.2H_2O$				
calculated	47.35	22.25	3.41	10.38	-
experimental	47.01	22.50	3.34	9.95	-

IR- and UV-Spectra

The Bomem-Michelson 100 spectrometer served as FTIR instrument. The solid state IR-spectra were taken as Nujol mulls. The technic in pells was not applicable because the complexes decomposed upon pressing in KBr. The IR-spectra of 0.0005 M *2-AP* solution in carbon tetrachloride (Merck, Uvasol) and those of the saturated water solution of *SAPPD* were obtained by using 5 cm quartz and 0.002 cm CaF_2 cells, respectively.

The UV-spectra were measured on a Specord UV-VIS spectrometer in 0.0001 M H_2O solution, 1 cm path length.

The length of the polynuclear chain of *SAPPD* in sulphuric acid solutions was obtained by the method of continuous variations [8]. The band

corresponding do the d→d transition of Pd^{2+} was used (λ_{max} = 417 nm, ε = 148 $cm^2.mmol^{-1}$) [9].

RESULTS and DISCUSSION

The following results are obtained in the comparative IR- and UV-spectral study:

1. The IR-spectrum of *SAPPD* reveals characteristic of a bidentate co-ordination splitting of the triply degenerate $\nu_3 SO_4$ mode, but without any absorption maxima at 1240-1200 cm^{-1} (Fig. 1.1), thus indicating a *bridging* co-ordination of the sulphate ions [7]. Moreover, the observed identity of the IR-spectral data both in water solution and in the solid state (Fig. 1.1 and Fig. 1.3), suggests a bridging co-ordination of SO_4^{2-} to Pd^{2+} in solution as well.

2. The comparison of the IR-spectra of *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ and *SAPPD* with *2-AP* in the NH_2 stretching region (3700-3100 cm^{-1}) is performed with a strongly dilute carbon tetrachloride solution of the latter in order to avoid its self-association effects. Under these conditions the IR-spectrum of 2-AP (Fig. 2.1) exhibits the bands at 3510 cm^{-1} ($\nu_{as}\ NH_2$) and 3408 cm^{-1} ($\nu_s\ NH_2$) corresponding to non-associated amino groups [10-12]. It is seen from Fig. 2.2 that the inclusion of *2-AP* in *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ provokes only a low-frequency shift of both the absorption maxima. New bands in 3300-3200 cm^{-1} range, typical of co-ordinated NH_2 group in Pd (II) aniline complexes [13] are not observed, indicating that *2*-AP amino group is not engaged in complex formation. In opposite, the

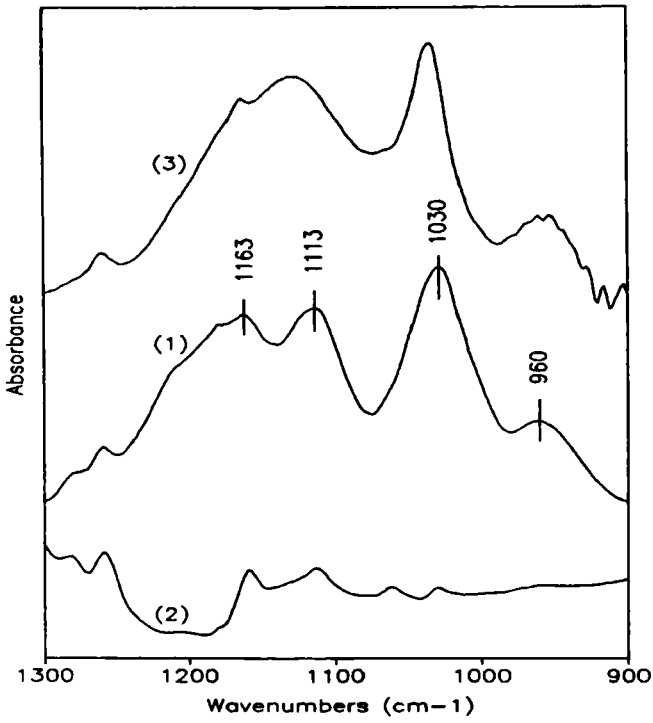


Fig. 1. IR-spectra in the 1300-900 cm^{-1} region: *SAPPD* (**1**) and *HAPPD* (**2**) - mulls in Nujol; *SAPPD* (**3**) - solution in H_2O

IR-spectrum of *SAPPD* consists of wide, overlapping bands with absorption maxima at 3420 cm^{-1}, 3190 cm^{-1} and 3110 cm^{-1} (Fig. 2.3). This strongly expressed difference in comparison with the spectrum of *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ is one of the arguments proving amino group co-ordination to Pd^{2+} in the sulphato complex.

3. The comparison of the IR-spectra of *SAPPD* and *HAPPD* in the regions 1300-900 cm^{-1} and 3700-3100 cm^{-1} (Figs. 1 and 2) indicating the absence of intensive *HAPPD* absorption bands in the first interval

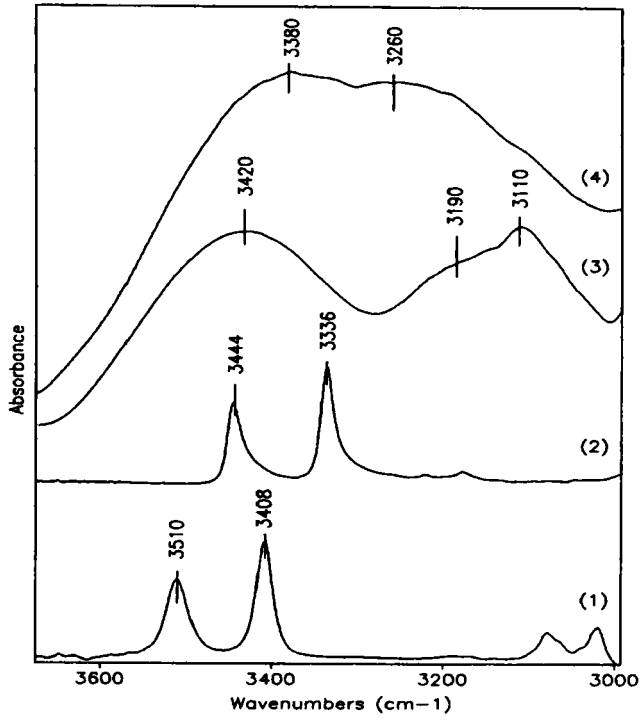


Fig. 2. IR-spectra in the NH_2 stretching region: *2-AP* (**1**) - solution in carbon tetrachloride; [*Pd(2-AP)*$_2$*Cl*$_2$] (**2**), *SAPPD* (**3**) and *HAPPD* (**4**) - mulls in Nujol

(Fig. 1.2) makes evident the substitution of SO_4^{2-} with OH^- ions. This exchange causes a strongly increasing absorption in the NH_2 stretching region at 3380 cm^{-1} and 3260 cm^{-1} (Fig. 2.4).

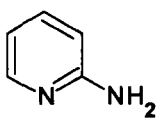
4. The comparative UV-spectral analysis shows that both the free ligand and *trans*-[*Pd(2-AP)*$_2$*Cl*$_2$] exhibit the typical for the pyridine system (**I**) *p*- and α-bands (Fig. 3.3 and 3.4) at 230 nm ($\varepsilon \sim 9500$ $cm^2.mmol^{-1}$) and 290 nm ($\varepsilon \sim 4000$ $cm^2.mmol^{-1}$), respectively [14]. Therefore, the

monodentate co-ordination through the nitrogen of the pyridine ring does not change the aromatic character of *2-AP* in the chloride complex.

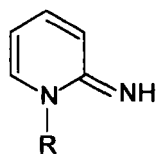
However, the bands at 230 nm and 290 nm are not observed in *SAPPD* and *HAPPD* spectra, where a new absorption maximum appears at 255 nm (Fig. 3.1 and 3.2). Two complement explanations of this phenomenon are possible and each of them confirms the bidentate co-ordination of *2-AP* as follows:

- The additional 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 same effect is observed by comparing the UV-spectra of aniline and its cation in H_2SO_4 solution [15].

- The band about 255 nm is characteristic of the pyridone-imine structure (**II**), which is observed in 1-methyl-2-pyridone-imine (**II**, R = CH_3) [14]. This form is typical of *2-AP* monocation where the positive charge is localized mainly at the amino nitrogen (**III**) [16]. The possibility for the stabilization of pyridone-imine structure in both the sulphato and hydroxo complexes (**II**, R = H) could be considered as the result of an electron density redistribution by additional Pd→N(amino) dative bond formation which also creates a partial positive charge at the exocyclic nitrogen.



(I)



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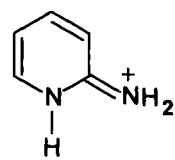

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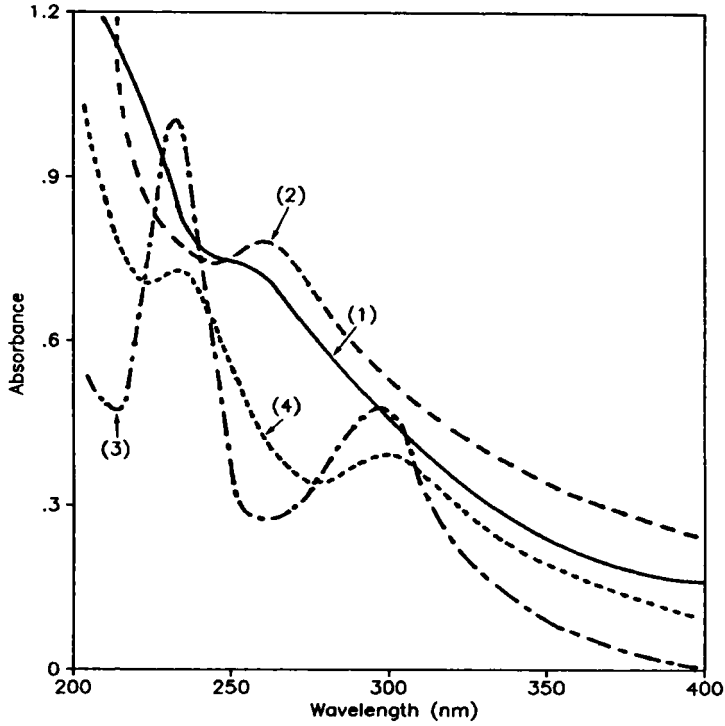
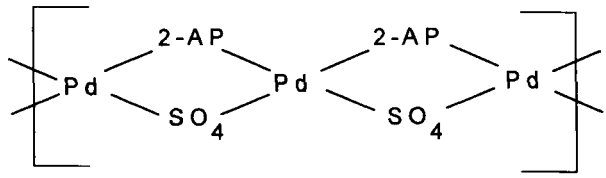


Fig. 3. UV-spectra of: *SAPPD* (**1**), *HAPPD* (**2**), *2-AP* (**3**) and [*Pd(2-AP)$_2$Cl$_2$*] (**4**); solutions in H_2O

The IR- and UV-spectral data reported above can be summarized as follows:

2-AP is bidentately co-ordinated in *SAPPD* both in solution and in the solid state. As a rule *2-AP* is a monodentate ligand, since the endocyclic nitrogen exhibits significantly stronger electron-donating power than the amino group [17]. The only compound in which *2-AP* is proved to co-ordinated as a bidentate ligand is [*Ag$_3$(2-AP)$_4$*](*NO$_3$*)$_3$ [18]. A decisive factor in this case is the linear co-ordination to Ag^+ and the formation of a quasi-

polynuclear complex as a result, with the participation of both the nitrogen atoms of the organic ligand. The situation is similar in *SAPPD* since the bridging SO_4^{2-} groups form a chain structure, in which Pd $^{2+}$ ions, co-ordinated with nitrogen of the pyridine ring are favourably oriented towards the amino group (Scheme **IV**). As a result of its bidentate co-ordination, *2-AP* stabilizes the oligomeric chain in solution as well.



(IV)

According to the method of continuous variations [8], in 4 M H_2SO_4 the ratio Pd : *2-AP* in *SAPPD* corresponds to five- or six- nuclear complex. On the ground of the results obtained about Pd $^{2+}$ co-ordination in higher than 3M H_2SO_4 [9], we consider that the outlying Pd $^{2+}$ ions of *SAPPD* (see Scheme **IV**) are co-ordinated with HSO_4^- and H_2O. When the complex is isolated in a solid state the weakly bonded HSO_4^- ions are hydrolytically substituted by OH^- ions. This could be the reason for the presence of the wide absorption maximum at 3420 cm^{-1} in the IR-spectra of *SAPPD* (Fig. 2.3). The data from the chemical analysis of *SAPPD* confirm the conclusions made above. The formation of six-nuclear complex corresponds to the formulae $[Pd_6(2\text{-}AP)_5(SO_4)_5](OH)_2.2H_2O$, which is in very good agreement with the experimental data (Table 1).

The identity of both *SAPPD* and *HAPPD* UV-spectra (Figs. 3.1 and 3.2) assumes that *2-AP* is bridging co-ordinated in *HAPPD* too. This suggests that the oligomeric structure remains when SO_4^{2-} is substituted by OH^-. Therefore, the hydroxo complex corresponds to the formulae $[Pd_6(2\text{-}AP)_5(OH)_{10}](OH)_2.2H_2O$, which is in good coincidence with the elemental analysis data (Table 1). The oligomeric structure of hydroxo-2-aminopyridine-palladium complex stabilized in this way determines the effective physical and chemical properties of the activation solution. This conclusion substantiates the necessity of two-steps preparation of the alkaline 2-aminopyridine-palladium activator.

ACKNOWLEDGEMENTS

The financial support from the National Foundation "Scientific Research" (Project X-310) is gratefully acknowledged.

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Date Received: May 1, 1997
Date Accepted: June 15, 1997