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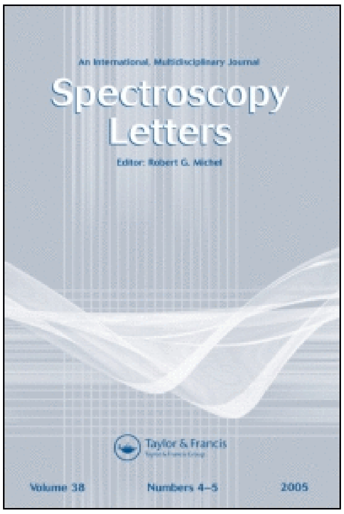

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IR-Spectral Study of 2-Aminopyridine and Aniline Complexes with Palladium (II)

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

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IR-SPECTRAL STUDY OF 2-AMINOPYRIDINE AND ANILINE COMPLEXES WITH PALLADIUM (II)

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

Sh. Dinkov and M. Arnaudov *

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

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ABSTRACT

An IR-spectral study of sulphato- and chloro complexes of palladium (II) with 2-aminopyridine and aniline, respectively, is reported. The results obtained confirm the bidentate co-ordination of both 2-aminopyridine and SO_4 group in the case of sulphato-2-aminopyridine-palladium (II) leading to polynuclear structure of the complex in solution. The comparative investigation of sulphato-dianiline-palladium (II) suggests that the self-dependent ability of the SO_4^{2-} ion for bridging co-ordination can stabilize chain-like complexes of palladium (II) only in the solid state.

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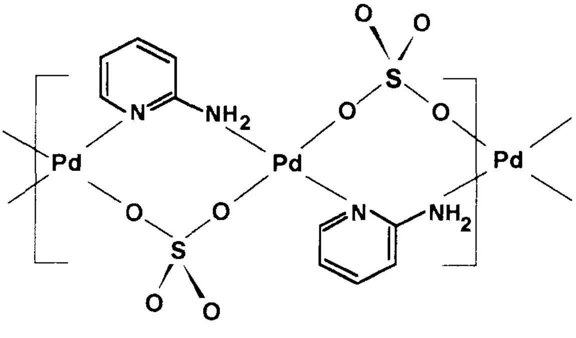
INTRODUCTION

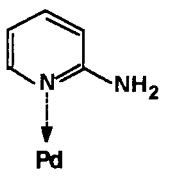
Our previous IR- and UV-spectral studies [1, 2] on the mechanism of the 2-aminopyridine (*2-AP*) complexation with Pd^{2+} show that when obtained in sulphuric acid solution sulphato-2-aminopyridine palladium (*SAPPD*) exhibits polynuclear structure as a result of bridging co-ordination of both the sulphato group and the organic ligand (**I**). This *2-AP* bidentate co-ordination is the reason that the complex keeps its oligomeric structure in alkaline medium, while the substitution of SO_4^{2-} with OH^- yields the hydroxo-2-aminopyridine palladium [1]. The latter complex has been utilized as the main component of activators used in currentless metalization of non-conducting surfaces [3, 4].



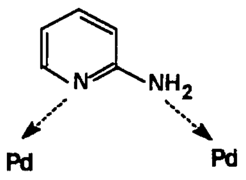
(I)

As a rule *2-AP* is monodentate ligand (**II**), since the endocyclic nitrogen exhibits significantly stronger electron-donating power than the amino group [5]. We have found out just one more instance with bridging *2-AP*-

complexation - $[Ag_3(2\text{-}AP)_4](NO_3)_3$[6], which is probably affected by the linear (digonal) Ag^+ co-ordination. Because of that, the *SAPPD* structure (**I**) was proved by careful IR- and UV-spectral studies, where the IR-spectral part of this research included a systematical comparison with the NH_2 characteristic bands of trans-dichloro-di-2-aminopyridine-palladium (*trans*-$[Pd(2\text{-}AP)_2Cl_2]$) exhibiting a monodentate *2-AP* co-ordination (**II**)[7]. However, the interpretation of the results was restricted by the slight-resolved *SAPPD* spectrum in 3600-3100 cm^{-1} range which is not suitable for NH_2 bands interpretation[1]. In the same way, the bending NH_2 mode (δ (NH_2)) appears in 1635-1600 cm^{-1} region by a low-intense peak additionally overlapping with the pyridine skeleton band[2].



(II)



(III)

In view of the reasons stated above, the results obtained are extended by a comparative IR-spectral analysis of *SAPPD* and *trans*-$[Pd(2\text{-}AP)_2Cl_2]$ towards the analogous complexes of aniline. This study is justified with the following purposes:

Under the precondition that the $Pd^{2+} \leftarrow NH_2$ bond formation is the single co-ordination mode in the case of Pd (II) complexes of aniline, an established similarity between the IR-spectra of *SAPPD* and sulphato-

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dianiline- palladium ([*Pd(An)$_2$SO$_4$*]) would give an immediate proof of the *2-AP* amino group participation in the *SAPPD* complexation. The next comparison between *trans-[Pd(2-AP)$_2$Cl$_2$]* and its aniline analogue trans-dichloro-dianiline-palladium (*trans-[Pd(An)$_2$Cl$_2$]*) should estimate the difference between the NH_2 bands shifting by an oblique (**II**) or a direct (**III**) *2*-AP amino group influence. Moreover, the IR-spectral confrontation of the sulphato- and chloro complexes should reveal the supplementary effect of NH...O=S hydrogen bond formation.

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EXPERIMENTAL

SAPPD, trans-[Pd(2-AP)$_2$Cl$_2$], trans-[Pd(An)$_2$Cl$_2$] and their NH_2 group deuterated derivatives were synthesized as previously described [1, 7, 8].

Sulphato-dianiline-palladium complex ([*Pd(An)$_2$SO$_4$*]) were prepared by mixing solutions of 1.42 g (0.005 mol) dianiline sulphate in 10 ml 5M H_2SO_4 to 1.192 g (0.005 M) $PdSO_4.2H_2O$ in 5 ml 5M H_2SO_4. The mixture was kept for 1 hour at 20° C, then 100 ml of absolute methanol are added. The obtained after 4 hours orange-red precipitate was filtrated, washed with methanol and dried by evaporation at 50° C.

Analysis: **Pd** - 27.3% (found), 27.4% (calc.); **$C_6H_5NH_2$** - 47.2% (found), 47.9% (calc.); **SO_4^{2-}** - 24.6% (found), 24.7% (calc.).

The NH_2-deuterated derivative of [*Pd(An)$_2$SO$_4$*] was obtained by reaction of amino-deuterated dianiline sulphate with $PdSO_4$ in 5M D_2SO_4 following the procedure stated above.

A Bruker Vector 22 FTIR-spectrometer served as an IR-instrument. The solid state spectra were taken as Nujol mulls. The technics in pells was non-applicable since the sulphato complexes decompose upon pressing in KBr. The spectra of both free ligands in carbon tetrachloride were recorded by means of 5 cm quartz cell (3600-3100 cm^{-1} range) and 0.01 cm KBr cell (1700-1500 cm^{-1}) for 0.0005 M and 0.05 M solute concentration, respectively. The saturated water solution of $[Pd(An)_2SO_4]$ was measured by using CaF_2-cell with 0.002 cm path length. The deconvolution of the spectra was performed with the program Spectra Calc.

The UV-spectra were obtained with a spectrometer Specord UV-VIS by means of 0.5 cm quartz cell . The Pd/aniline ratio in water solution of $[Pd(An)_2SO_4]$ was determined by the method of the continuous variation [9] using the UV-spectral band at 293 nm (see Fig. 6).

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RESULTS AND DISCUSSION

The comparison between the IR-spectral data of *trans*-$[Pd(An)_2Cl_2]$ and the free aniline (Table 1) shows the affecting of the NH_2 stretching frequencies by a $Pd^{2+} \leftarrow NH_2$ bond formation. *Trans*-$[Pd(An)_2Cl_2]$ exhibits three absorption maxima in the 3300-3100 cm^{-1} range (Fig. 1.1) which these at 3286 cm^{-1} and 3203 cm^{-1} have been assigned to the antisymmetric ($\nu_{as}(NH_2)$) and symmetric ($\nu_s(NH_2)$) stretching modes, respectively [8]. In fact, as in the IR-spectrum of liquid aniline [10], a Fermi resonance interaction between the symmetric NH_2 stretch and the overtone of $\delta(NH_2)$ is present causing a $\nu_s(NH_2)$ band splitting at 3203 cm^{-1} and 3120 cm^{-1} (Fig. 1.1). The unperturbed $\nu_s(NH_2)$ and $2\delta(NH_2)$ frequencies of *trans*-$[Pd(An)_2Cl_2]$ can be calculated [11] and the obtained value of 3178

Table 1

NH_2 frequencies (cm^{-1}) of the investigated chloro complexes and of the corresponding free organic ligands

Compound	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\Delta\nu(NH_2)$ [a]	$\delta(NH_2)$
Aniline [b]	3485	3398	87	1619
trans-[$Pd(An)_2Cl_2$] [c]	3286	3178 [d]	108	1573
2-Aminopyridine [b]	3510	3408	102	1621
trans-[$Pd(2\text{-}AP)_2Cl_2$] [c]	3444	3336	108	1597

[a] $\Delta\nu(NH_2) = \nu_{as}(NH_2) - \nu_s(NH_2)$.

[b] Dilute solution in carbon tetrachloride, see also Refs. [2, 12-14]

[c] Nujol mull

[d] Calculated according to Ref. [11] value

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cm^{-1} should be assigned to the symmetrical NH_2 frequency (Table 1). The second estimated frequency at 3145 cm^{-1} exactly coincides with $\delta(NH_2)$ overtone (2 x 1573 = 3146 cm^{-1}, Table 1).

Therefore, compared to the NH_2 stretch data of aniline (Table 1), the corresponding bands of *trans*-[$Pd(An)_2Cl_2$] are approximately 200 cm^{-1} low-frequency affected, and the shift due to complexation is additionally provoked by a weak NH...Cl interaction. Such a suggestion is in accordance with the results for the obtained $\Delta\nu(NH_2)$ values - the 87 cm^{-1} difference established in the case of the free aniline increases to 108 cm^{-1}

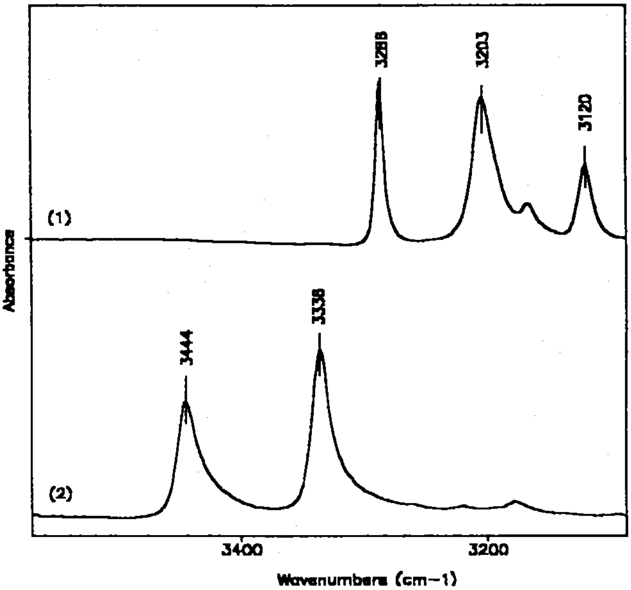

Fig. 1. 3600-3100 cm^{-1} IR-spectra (Nujol mulls) of: *[$Pd(An)_2Cl_2$]* (**1**) and *[$Pd(2\text{-}AP)_2Cl_2$]* (**2**)

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in the IR-spectrum of the complex (Table 1). This increment of 21 cm^{-1} is typical of a weak hydrogen bond formation where only one NH_2 group H-atom is involved [15, 16]. The X-ray analysis of *trans*-[$Pd(An)_2Cl_2$] confirms this assumption [17].

The next juxtaposition of the NH_2 stretching frequencies of *2-AP* and *trans*-[$Pd(2\text{-}AP)_2Cl_2$] (Table 1 and Fig. 1.2) demonstrates the NH_2 band influence caused by the indirect effect of *2-AP* monodentate complexation (Scheme **II**). The monomeric *2-AP* exhibits $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands at 3510 cm^{-1} and 3408 cm^{-1}, respectively, which are by 70 cm^{-1} low-frequency shifted in *trans*-[$Pd(2\text{-}AP)_2Cl_2$]. No indication about NH...Cl hydrogen bond formation is present since the $\Delta\nu$ *(NH$_2$)* value of the complex is almost the same as this of the free *2-AP* (Table 1). A final comparison with the corresponding data of *trans-*[*Pd(An)$_2$Cl$_2$*] suggests that the supplementary amino group inclusion by *2-AP* complexation (**III**) could result in more than 100 cm^{-1} extra shift of the NH_2 stretching bands.

The NH_2 scissoring frequencies of the discussed compounds are listed in the last column of Table 1 which the corresponding bands of the complexes are identified by their decrease in intensity on deuteration (Fig. 2). The data obtained are in agreement with the results of NH_2 stretching region. The NH_2 scissoring frequency of *trans-*[*Pd(An)$_2$Cl$_2$*] is lowered to 1573 cm^{-1} (Fig. 2.1, see also Ref. [8]), illustrating the supplementary polarization of NH bonds by the $Pd^{2+} \leftarrow NH_2$ bond formation. The comparison with the δ *(NH$_2$)* value of the free ligand shows a low-frequency shift of 46 cm^{-1}. This difference is reduced to 24 cm^{-1} in the case of the *trans-*[*Pd(2-AP)$_2$Cl$_2$*] (Table 1 and Fig. 2.2), where the *2-AP* amino group is indirect perturbed by the complexation (**II**).

The corresponding sulphato complexes are discussed in the same way. The 3600-3100 cm^{-1} IR-spectra of *SAPPD* and [*Pd(An)$_2$SO$_4$*] are given in Fig. 3. Their comparison establishes a similarity of both spectral curves below 3250 cm^{-1}, thus confirming the $Pd^{2+} \leftarrow NH_2$ bond formation in *SAPPD*. The solid state *SAPPD* spectrum exhibits an additional band at 3420 cm^{-1} (Fig. 3.2), which we have assigned to the $\nu(OH^-)$ and $\nu(H_2O)$ frequencies of the outlying units of the oligomeric chains [1]. The absence of this absorption maximum in the [*Pd(An)$_2$SO$_4$*] IR-spectrum (Fig. 3.1) is in accordance with the chemical analysis data of the isolated aniline complex which are showing no presence of water or hydroxylic groups in it.

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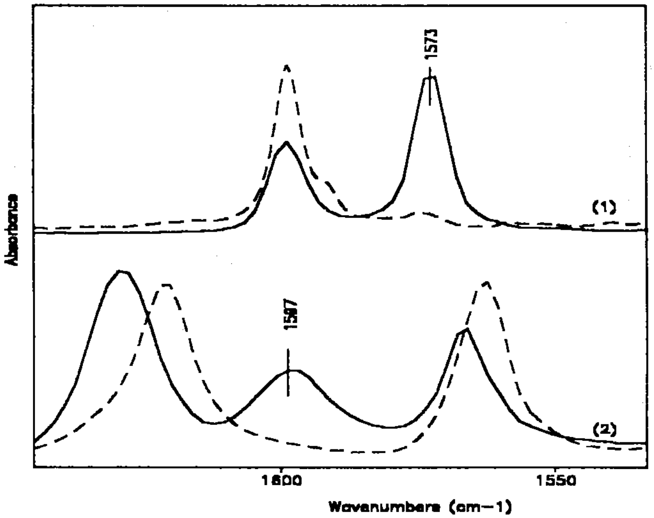

Fig. 2. 1700-1500 cm^{-1} IR-spectra (Nujol mulls) of: —— [*Pd(An)$_2$Cl$_2$*] (**1**) and [*Pd(2-AP)$_2$Cl$_2$*] (**2**); ----- amino-deuterated derivatives

The specifying deconvolution of the 3300-3100 cm^{-1} region (dotted lines in Fig. 3) resolves series of absorption maxima which are partially overlapped in both spectra. However, two observable distinctions are evident: (i) the [*Pd(An)$_2$SO$_4$*] spectrum exhibits additional peaks in the 3300-3240 cm^{-1} range (Fig. 3.1); (ii) the most-intense absorption maxima in the *SAPPD* spectrum are shifted to 3100 cm^{-1} overlapping with ν *(C-H)* bands of the pyridine ring (Fig. 3.2). The connection of these data with the effect of NH...O=S hydrogen bond formation is clearly illustrated by an analysis of the 1650-1550 cm^{-1} spectra of both complexes.

In this region [*Pd(An)$_2$SO$_4$*] exhibits two bands attributed to the δ *(NH$_2$)* frequencies (Fig. 4.1). This fact should be explained with formation of the

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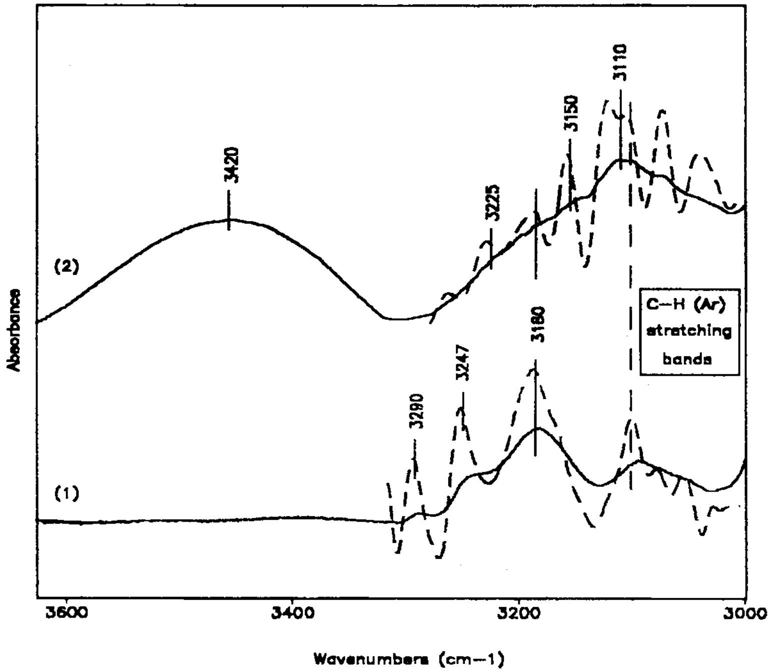

Fig. 3. 3600-3000 cm^{-1} IR-spectra (Nujol mulls) of : —— *[Pd(An)$_2$SO$_4$]* **(1)** and *SAPPD* **(2)**; ----- accordingly deconvoluted spectra

polymeric structure (**IV**) in the solid state which affords the realization of a NH...O=S interaction between SO$_4$ $^{2-}$ ion and *one* of the amino groups belonging to the same unit of the chain. The high-frequency band at 1615 cm^{-1} should be assigned to this δ *(NH$_2$)* mode whereas the NH$_2$ scissoring frequency of the second amino group, unperturbed by hydrogen bond formation, occurs at 1570 cm^{-1} (Fig. 4.1). It is noteworthy, that the latter value as well as the peak at 3290 cm^{-1} are very close to the δ *(NH$_2$)* and ν_{as} *(NH$_2$)* frequencies, respectively, of the *trans*-*[Pd(An)$_2$Cl$_2$]* (Table 1),

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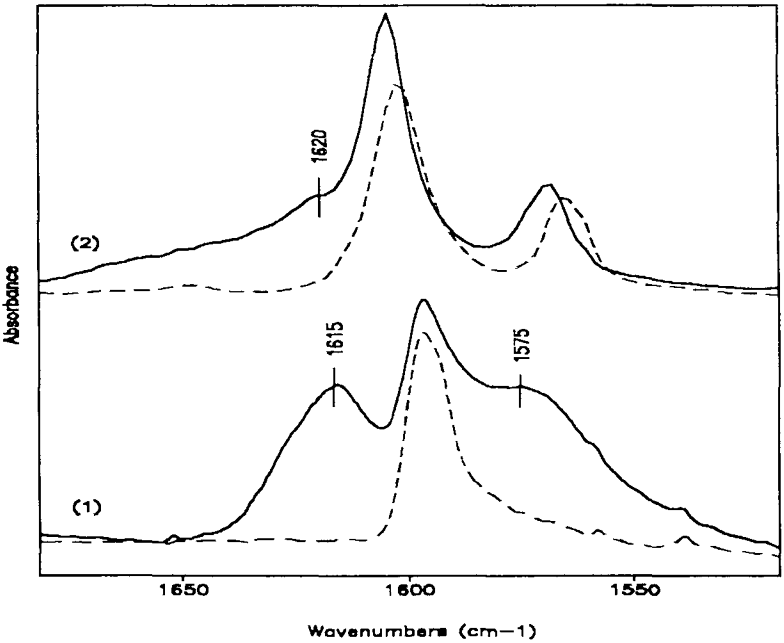
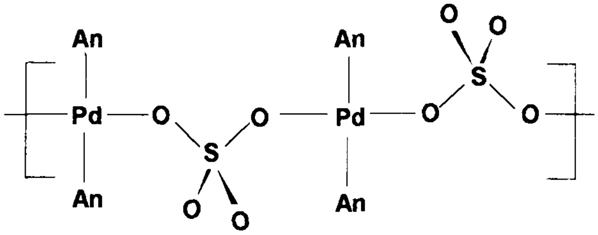


Fig. 4. 1700-1500 cm^{-1} IR-spectra (Nujol mulls) of : —— $[Pd(An)_2SO_4]$ (**1**) and *SAPPD* (**2**); ----- amino-deuterated derivatives

where only the weak NH...Cl interaction affects one of the NH bonds. In the case of *SAPPD*, where *2-AP*/SO_4^{2-} ratio is 1:1, all NH_2 groups should be hydrogen bonded and the 1650-1550 cm^{-1} spectrum shows a single δ (NH_2) band at 1620 cm^{-1} (Fig. 4.2). This possibility is in accordance with the strong low-frequency shift of the corresponding ν (NH_2) bands to 3100 cm^{-1} (Fig. 3.2), caused by a stable NH...O=S hydrogen bond formation.



(IV)

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The conclusions stated above are based on the suggestion that the sulphato groups in both complexes are bridging co-ordinated forming the polynuclear structures (**I**) and (**IV**), respectively. In regard to *SAPPD*, the latter assumption is proved by the study of the 1300-900 cm^{-1} region where the IR-spectrum reveals characteristic splitting of the triply degenerate ν_3 (SO_4) mode [1], due to bridging co-ordination of the sulphato ions (see also Ref. [18]). The $[Pd(An)_2SO_4]$ complex is investigated in the same way and a similarity with *SAPPD* spectrum is established (Fig. 5.1). This proves the stabilization of the polynuclear structure (**IV**) in the solid state. The appearance of the low-intense peaks in the 1240-1200 cm^{-1} range (Fig. 5.1), should be refereed to a chelating co-ordination [18] of the outlying SO_4 groups limiting oligomeric chains at a given length.

However, the study of 1300-900 cm^{-1} IR-spectra of both sulphato complexes in water solution reveals one fundamental difference between their properties. In this region *SAPPD* exhibits the same peaks as in solid state [1] (Fig. 5.2). Contrariwise, the band splitting disappears in the case of $[Pd(An)_2SO_4]$ demonstrating only one broad band at 1105 cm^{-1} (Fig. 5.1), typical of the degenerate ν_3 (SO_4^{2-}) mode of free sulphato ions in

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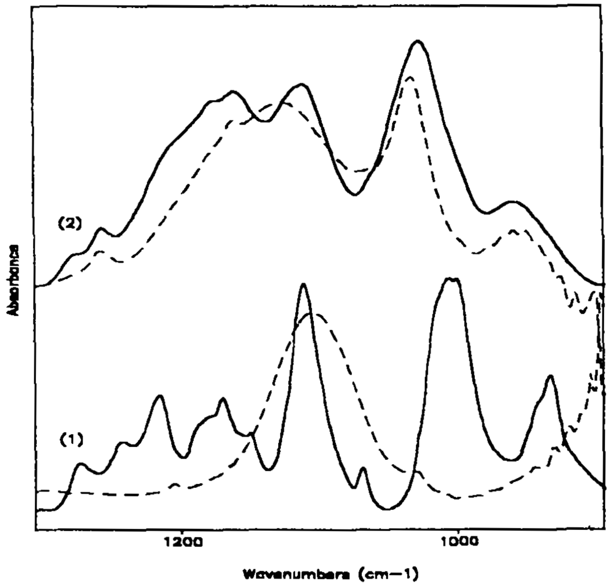

Fig. 5. 1300-900 cm^{-1} IR-spectra of : [*Pd(An)*$_2$*SO*$_4$] (**1**) and *SAPPD* (**2**);
—— solid state (Nujol mull); ----- solution in H_2O

aqueous solution. This result indicates a breaking of the oligomeric chains attended by a replacement of the SO_4^{2-} ions by OH^- and H_2O thus forming mononuclear aquahydroxo complexes. The latter assumption is suggested through the UV-spectral investigation of [*Pd(An)*$_2$*SO*$_4$] in diluted water solution (pH = 3). The spectrum does not exhibit the bands characteristic of the free aniline (Fig. 6), thus proving the presence of the complex(es) between aniline and Pd (II). The next analysis by the method of the continuos variations [9], accomplished at the same experimental conditions, verifies that the Pd/aniline ratio corresponds to 1:2.

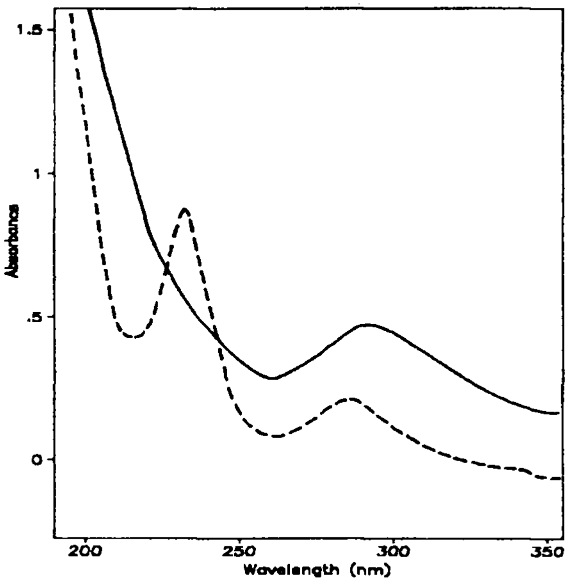

Fig. 6. UV-spectra of: —— *[Pd(An)$_2$SO$_4$]* and ----- aniline, 0.0026 M and 0.0002 M solution in H_2O, respectively

The recapitulation of the results obtained confirms the presence of an additional $Pd^{2+} \leftarrow NH_2$ dative bond in sulphato-2-aminopyridine-palladium (II). Its formation is due to the SO_4^{2-} bridging co-ordination in the solid state, thus building polynuclear chains in which Pd^{2+} ions are favourably oriented towards both the *2*-AP nitrogen atoms. Because of this combination of two bridging bonds the complex keeps its oligomeric structure in water solution too. The comparative study of *[Pd(An)$_2$SO$_4$]* illustrates that the self-dependent ability of the SO_4 group for bridging co-ordination can stabilize chain-like complexes with palladium (II) only in the solid state.

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