FORMATION OF ACETATO COMPLEXES OF PALLADIUM(II) IN AQUEOUS AND NON-AQUEOUS MEDIUM

Lidija Šoptrajanova and **Ilinka Spirevska**

Institute of Chemistry, The "Sv. Kiril i Metodij" University,
P. O. B. 162, 91001 Skopje, Macedonia

The reactions leading to the formation of acetate complexes of palladium(II) were studied in aqueous and non-aqueous media. Complexation apparently takes place in both cases. The formation of complexes (acetato or mixed) with an average number of ligands close to 4 is indicated for the aqueous solutions. The addition of a sodium acetate solution to palladium acetate dissolved in glacial acetic acid leads to the formation of disodium hexaacetatodipalladium. The infrared spectrum of the product obtained in this latter case is recorded.

Key words: palladium; acetates; complexes; glacial acetic acid; UV spectroscopy; IR spectroscopy; potentiometry

INTRODUCTION

Among the palladium compounds (both simple and complex), the most numerous are those of palladium(II). As far as the *complexes* of palladium(II) are concerned, the majority of the published studies are devoted to compounds in which soft bases act as ligands. It should be recalled that according to the Pearson's [1−3] classification, the *soft* bases contain easily oxidizable electron-donor atoms with low electronegativity and high polarizability (e.g. R_3P, R_3As, CN^-, CO etc.). On the other hand, the *hard* bases contain donor atoms which have high electronegativity, low polarizability and are difficult to oxidize. Ligands such as H_2O, OH^-, CH_3COO^-, NH_3, RNH_2 etc. fall into this latter class.

Since the palladium cations are considered as *soft* acids, the complexes with *soft* bases should be, according to the Pearson's HSAB principle [1−3], more stable than those with *hard* bases. This is, most probably, the reason behind the considerably higher number of investigated palladium complexes with *soft* bases as compared with those containing *hard* bases as ligands.

Nevertheless, complexes of palladium(II) with *hard* bases are known, the complexes with acetates as ligands falling into this category. The study of such complexes dates back to 1965 when Stephenson et al. [4] published a method for the preparation of palladium(II) acetate and a number of its adducts, mainly of the $[Pd(CH_3COO)_2L_2]$ type where L is triphenylarsine, triphenylphosphine, pyridine or 2,2'-bipyridine. Complexes of the $[Pd(CH_3COO)_2L]_2$ type where L is phenylphosphine or phenylarsine were also reported [5].

The preliminary account of the determination of the palladium(II) acetate crystal structure was published by Skapski and Smart [6] who found that the composition and structure of the crystals studied by them could be best described as $2[Pd_3(CH_3COO)_6 \cdot H_2O$. The structures of other similar compounds (but containing benzene or dichloromethane instead of water) were later determined by Cotton and Han [7, 8] and Barton *et al.* [9]. In these complexes, all acetate ions (or, perhaps more precisely, all acetato ligands) have a *bridging* function.

Brandon and Claridge [10] synthesized complexes of the $M_2[Pd(CH_3COO)_4] \cdot x H_2O \cdot y CH_3COOH$ type (where M^{2+} is a cation of metals such as Ca, Cu, Ni or Ba). These complexes are soluble in water but, undergoing hydrolysis reactions, decompose, leaving $Pd(OH)_2$ as the final product. Pandey and Henry [11] reported that $M_2[Pd_2(CH_3COO)_6]$ and $M_2[Pd(CH_3COO)_4]$ complexes (M = Na or Li) are formed in a glacial acetic acid medium, but failed to isolate them.

A large part of our own work in the last two decades or so has been devoted to the study of palladium acetate complexes. Our first attempts in this field were directed towards the preparation of tetra-acetatopalladium(II) complexes and, as far as possible, the estimation of their stability constants [12−14].

The results obtained later on and devoted to the synthesis of acetato complexes from palladium(II) perchlorate in aqueous solutions and from trimeric palladium(II) acetate in glacial acetic acid will be summarized in the present paper. Some of them have been briefly reported [15−16].

EXPERIMENTAL

Solutions and reagents

The solution of palladium(II) perchlorate was prepared using the method described by Tempelton *et al.* [17] and was standardized according to Vogel [18].

Solid palladium(II) acetate was prepared following the method of Stephenson *et al.* [4].

The solutions of sodium acetate and of acetic acid were standardized by potentiometric methods.

Methods

In order to establish the conditions under which the acetato complexes of palladium are formed, a series of solutions with a constant palladium(II) concentration and a varying concentration of the acetate ligands were prepared.

In *aqueous medium* the initial concentrations of palladium(II) perchlorate and of acetic acid in the solution were $9.98 \cdot 10^{-4}$ mol dm^{-3} and 8.0 mol dm^{-3} respectively. Solid sodium acetate was added to portions of such a solution and this caused the pH value of the system to change from 0.41 to 5.76. Alternatively, to aliquots of a palladium perchlorate solution (in which the solute concentration was initially $4.43 \cdot 10^{-5}$ mol dm^{-3}), portions of a sodium acetate solution were added so that the palladium-to-acetate mole ratio varied from 1 : 45 to 1 : 1800 and the pH values were close to 3. The initial concentration of sodium acetate in its solution was 1.0 mol dm^{-3}.

In *glacial acetic acid medium,* the initial solutions were those of palladium(II) acetate [with $c(Pd) = 2.0.10^{-3}$ mol dm^{-3}] and of sodium acetate (the acetate concentration was 4.0 mol dm^{-3}). A series of solutions was prepared in which the palladium concentration was constant and the Pd : OAc mole ratios varied from 1 : 2 to 1 : 500.

The ultraviolet spectra of all solutions containing palladium and acetates were recorded 10 minutes after the aliquots of the initial solutions were mixed and then at 30 min intervals up to a period of twelve hours.

In the following seven days the spectra were recorded at 48 hr intervals and then once per week, until the end of a total period of three months.

In order to determine the average number of acetate ligands using the Leden's method [19], a series of Pd(ClO$_4$)$_2$ solutions containing a variable quantity of an acetate buffer solution was prepared. The solute concentration was $5.7 \cdot 10^{-4}$ mol dm^{-3} and the Pd : OAc$^-$ mole ratio varied from 1 : 100 to 1 : 1450.

The charge of the complex ions formed in the course of the reaction in glacial acetic acid medium was determined by high-voltage paper electrophoresis. The results have been published [15].

On slow evaporation of the solvent *in vacuo,* from the solution in glacial acetic acid in which the palladium-to-acetate mole ratio was 1 : 100, colorless crystals of sodium acetate separated first, to be covered, later on, by dark orange crystals of the formed complex. The sharp difference in the color made it possible to separate them mechanically and to obtain crystals of the reaction product with satisfactory purity.

The complexes formed in the course of the reaction carried out in aqueous medium were impossible to isolate as pure solids.

Apparatus

The UV-VIS spectra were recorded using a Perkin-Elmer 137UV and a Beckman DB-GT instrument, whereas the infrared spectra were obtained on a Perkin-Elmer 521 spectrophotometer.

The potentiometric measurements were performed on a Radiometer PHM 26 instrument. For the measurements of the palladium(2+) ion concentrations, the pH-meter was provided with a palladium working electrode, whereas in the case of the pH measurements a glass electrode was used. All potentiometric measurements were done against a saturated calomel electrode used as a reference. The reproducibility was ± 0.2 mV, i.e. 0.002 pH units.

RESULTS AND DISCUSSION

Formation of complexes in aqueous solution

The UV-VIS spectrum of a Pd(ClO$_4$)$_2$ solution in perchloric acid (the salt concentration being $9.98 \cdot 10^{-4}$ mol dm^{-3}) is shown in Fig. 1 (curve 1). As seen, it consists of only two rather ill-defined bands. Rather dramatic changes occur on addition of an aqueous acetic acid solution (the concentration of the acid in this solution was 8.0 mol dm^{-3}), although the pH value changes only negligibly (from 0.41 to 0.47). Namely, the band at shorter wavelengths, disappears, whereas that at longer wavelengths gains in intensity and

becomes much better defined, its maximum being close to 380 nm (*cf.* Fig. 1, curve 2).

On addition of NaOH to the Pd(ClO$_4$)$_2$ solutions in acetic acid, the pH value increases, reaching 5.76 and, simultaneously, the concentration of the acetate ions also goes up. It should be pointed out that, despite the high pH values in some of the solutions, Pd(OH)$_2$ does not separate, although the formation of a precipitate could have been expected [20].

When acetate ions *are* present, the changes in the appearance of the UV-VIS spectra parallel those in the
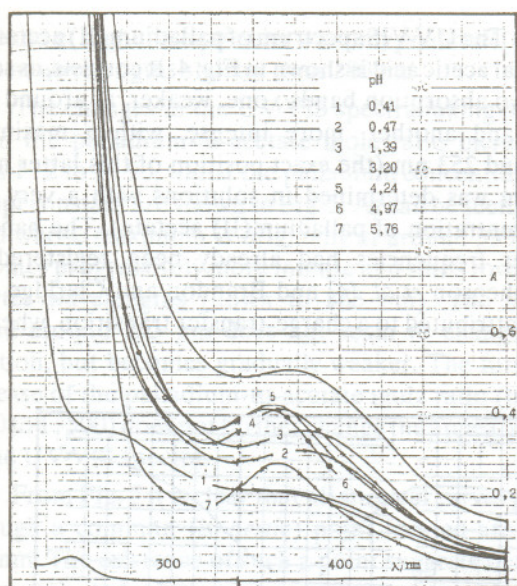
Fig. 2 – UV-VIS spectra of an aqueous solution of $Pd(ClO_4)_2$
(curve 1); of an analogous solution containing acetic acid
(curve 2) and of solutions with varying concentrations of NaOH
(curves 3–7). In all cases $c(Pd) = 9.98 \cdot 10^{-4} \, mol \cdot dm^{-3}$

pH values (Fig. 1, curves 3–7), the band at around 380
nm gaining in intensity and shifting towards shorter
wavelengths. Contrary to that, in the *absence* of acetate
ions, the analogous changes in the pH values of the
solution not only result in spectra (Fig. 2) which are
different from those shown in Fig. 1, but (in accordance
with the expectations [20]) $Pd(OH)_2$ precipitates at pH
values higher than 1.54.

In the solutions containing acetates, some sort of
complexation reaction between the palladium(2+)
and acetate ions is thus likely to occur. Is not entirely
clear whether such a reaction leads to the formation of
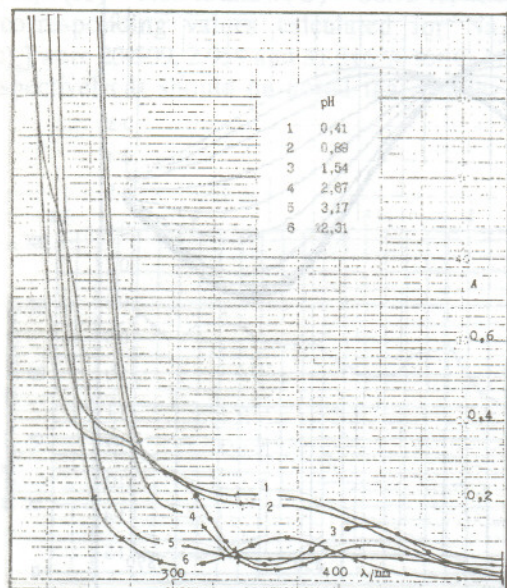
Fig. 2 – UV-VIS spectra of an aqueous solution of $Pd(ClO_4)_2$
(curve 1) and of solutions with varying concentrations

complexes containing only acetato ligands or of mixed
complexes containing acetato and hydroxo ligands.
That complexes are indeed formed and that they are
negatively charged was proven by our high-voltage
electrophoresis studies [15]

An alternative course of study was also followed.
As mentioned above, instead of changing the pH
values, the palladium-to-acetate mole ratios were
varied, keeping the pH values close to 3. The changes
in the appearance of the UV-VIS spectra (shown in Fig.
3) are quite similar to those represented in Fig. 1, so
that reactions leading to similar equilibria are ex-
pected to take place in the two cases. The electro-
phoretic studies [15] lent additional support to such an
assumption, since the complex containing palladium
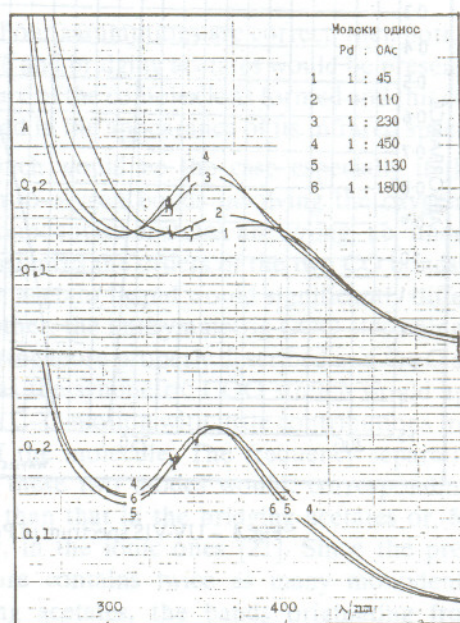again migrated towards the anode.

Fig. 3 – UV-VIS spectra of aqueous of $Pd(ClO_4)_2$
in which pH = 3, $c(Pd) = 4.43 \cdot 10^{-4} \, mol \cdot dm^{-3}$ and
the $Pd : OAc^-$ mole ratios vary from 1 : 45 to 1 : 1800

The results of the electrophoretic studies were
further corroborated by the determination of the
average number of acetato ligands per palladium
cation. The graphical method of Leden [19], namely, a
value of 3.8 for this number, fully in line with the
negative charge of the complex ion containing pal-
ladium as found by electrophoresis.

Since the above value for the average number of
ligands is close to 4 and since the only available anions
are the acetate (OAc^-) and the hydroxide (OH^-) ones,
the composition of the complex ions formed in aque-
ous solution (if they are mononuclear) could be
represented as $[Pd(OAc)_4]^{2-}$, $[Pd(OAc)_3OH]^{2-}$,
$[Pd(OAc)_2(OH)_2]^{2-}$ or $[Pd(OAc)(OH)_3]^{2-}$. It is, of
course, also possible that more than one species is
formed and/or that the complexes are polynuclear.

Formation of complexes in glacial acetic acid

The situation is better defined and the results are easier to interpret in the case of the complexes formed from palladium(II) acetate and sodium acetate in a glacial acetic acid medium since, in addition to the sodium cations, only "suitable" (palladium and acetate) ions or their combinations are present in this case. It should be recalled that palladium(II) acetate crystals are *trinuclear* and, as shown by Stephenson *et al.* [4], the trimers persist in glacial acetic acid solution as well.

The UV-VIS spectrum of palladium(II) acetate in glacial acetic acid is shown in Fig. 4. It consists, as seen, of two absorption bands : one, weaker, at around 399 nm and another, more intense, with a maximum around 253 nm (the exact position of this latter maximum was determined in solutions with a very low concentration of palladium(II) acetate). The band at lower frequencies had already been registered by Stephenson *et al.* [4] and Brandon and Claridge [10] and attributed to a charge-transfer transition, whereas
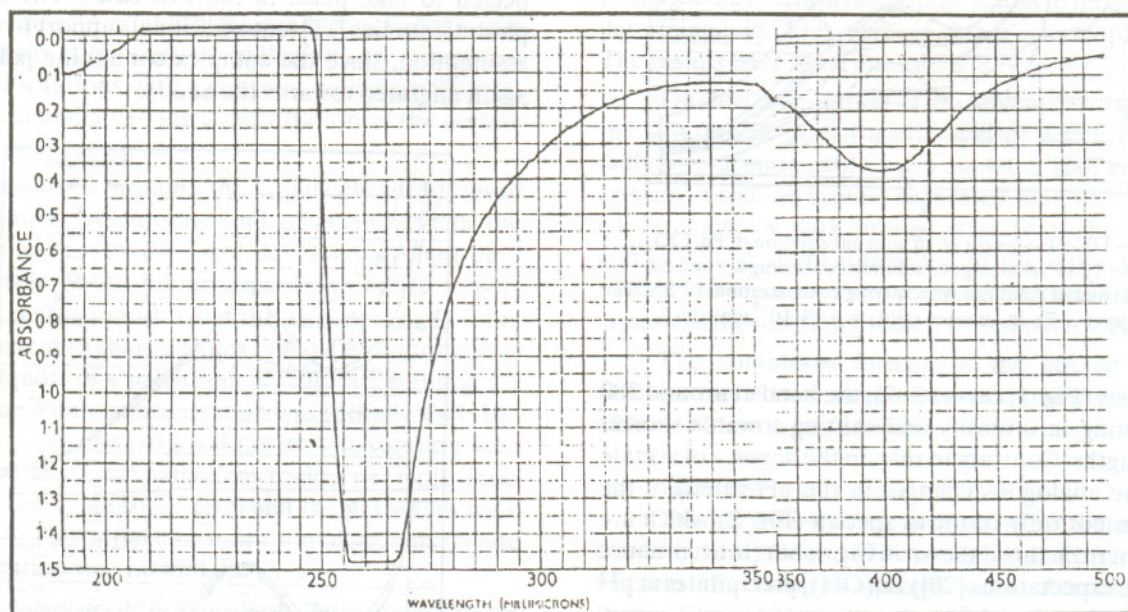
Fig. 4 – UV-VIS spectrum of $Pd(OAc)_2$ in glacial acetic acid $[c(Pd) = 4.0.10^{-4} \text{ mol d}^{-3}]$
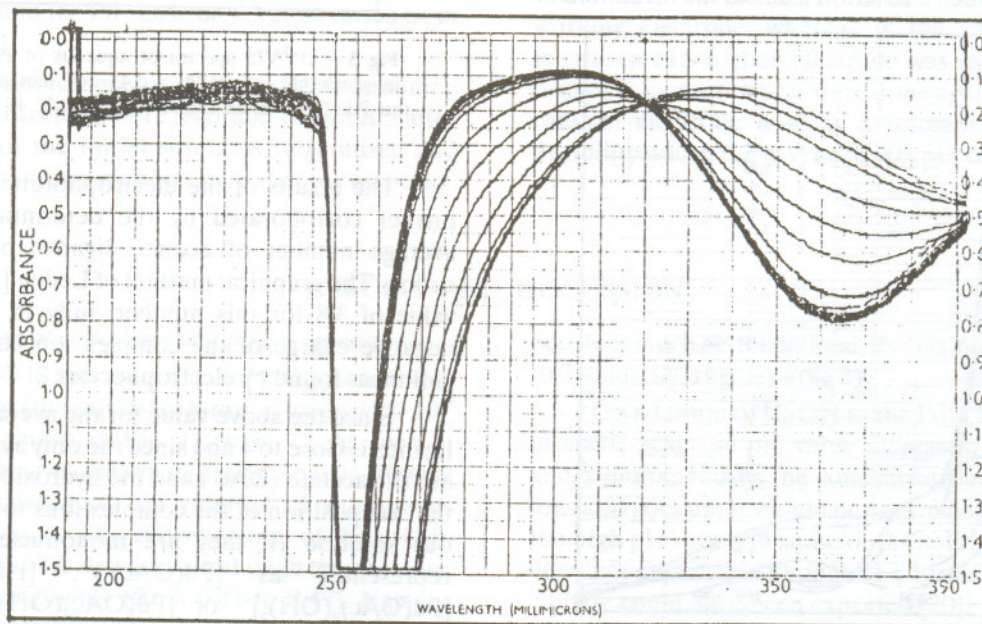
Fig. 5 – UV-VIS spectra of $Pd(OAc)_2$ and NaOH in glacial acid
(the Pd : OAc⁻ mole ratios vary from 1 : 2 to 1 : 500)

the band at higher frequencies was only *predicted* [4] to exist at wavelengths shorter than 280 nm.

The changes in the UV-VIS spectra taking place when the palladium-to-acetate mole ratio increases from 1 : 2 to 1 : 90, whilst the palladium concentration is kept constant are shown in Fig. 5. As can be seen, the band whose maximum is originally at around 399 nm becomes progressively more intense and shifts towards shorter wavelengths (down to 365 nm). The band found around 253 nm does not seem to change its position, but becomes gradually weaker. The further increase of the palladium-to-acetate mole ratio (from 1 : 90 to 1 : 500) does not further change the appearance of the UV-VIS spectra.

From Fig. 5 it is clear that all spectral curves pass through a common (*isobestic*) point located around 322 nm. The existence of such a point suggests that in the investigated solutions an equilibrium is established between *two molecular species* capable of absorbing the electromagnetic radiation in the studied region. The first of these two species is undoubtedly the original palladium(II) acetate compound, whereas the second one is, apparently the product of the reaction between palladium(II) acetate and sodium acetate. That this is indeed the case was again shown by the electrophoretic measurements, the palladium containing compound migrating towards the anode [15].

Taking into account the data presented above, a reasonable assumption would be that the reaction between hexaacetatotripalladium molecules and acetate ions leads to the formation of hexaacetatodipalladium(2–) ions. The results of the elemental analysis of the mechanically separated reaction product support such an assumption, i.e. it was found that the mass fractions of carbon, hydrogen and oxygen were $w(C) = 23.39 \%$, $w(H) = 3.03 \%$ and $w(O) = 30.98 \%$, whereas the corresponding values calculated for $Na_2[Pd_2(OAc)_6]$ were 23.509, 2.959 and 31.316 % for C, H and O respectively. It should be noted that Pandey and

Henry [11], as briefly mentioned above, also postulated the formation of $M_2[Pd_2(OAc)_6]$ complexes but did not isolate them.

In view of the usual tendency of palladium(II) to form square-planar complexes, the probable structure of these ions could be represented by the formula:
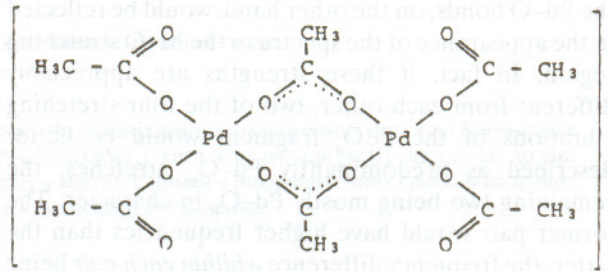
If our assumptions are correct, then both monodentate and bridging acetates would be present in the structure of the complex ions formed and this could be reflected in the appearance of its infrared spectrum.

Such would be the case especially if the palladium-to-oxygen bonds involving the oxygens from the monodentate acetates are *strong*, i.e. under such circumstances the orders of the two CO bonds within a given acetato ligand would significantly differ from each other, the antisymmetric COO stretching vibration being more properly described as a C=O stretch, whereas the symmetric COO stretch would approximate a C–O motion with little contributions from the rest of the molecule. The frequency separation between these two modes would, correspondingly, be larger than that in the bridging acetates or, for that matter, in the ionic ones [21]. Since the presumed structure contains twice as many monodentate as bridging acetates, the bands originating from the vibrations of the former type of ligands should be appreciably stronger than those which are due to the modes of the bridging acetates.
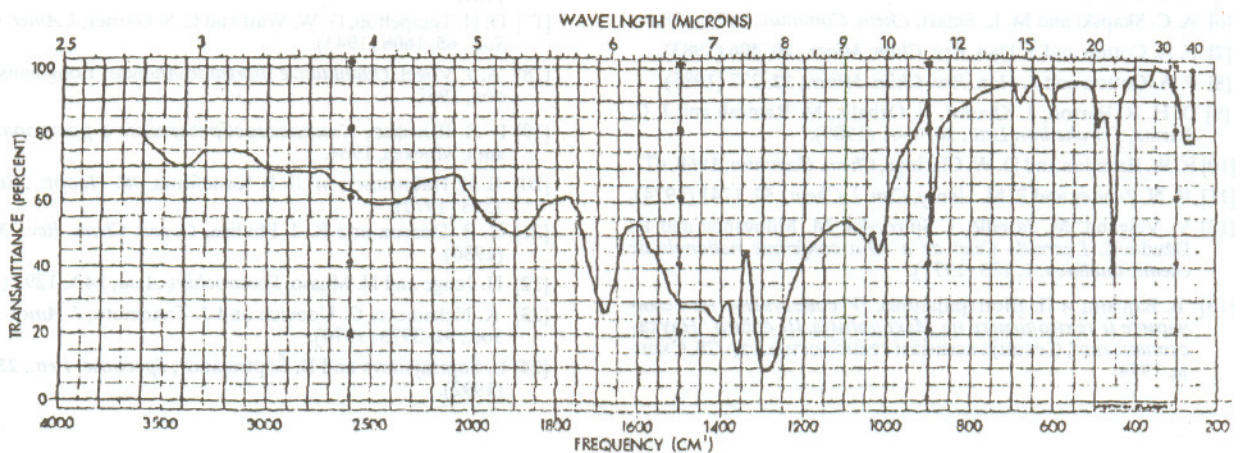
As mentioned, the differences between the carboxylic vibrations of the two types of acetates would be more pronounced if the strength of the Pd–O_m bonds *exceeds appreciably* that of the Pd–O_b ones (the subscripts m and b stand for *monodentate* and *bridging* respectively, the attributes being related to the *acetates* and their bonding function and not to the oxygen atoms themselves). The differences in the strength of the Pd–O bonds, on the other hand, would be reflected in the appearance of the spectra in the M–O stretching region. In fact, if these strengths are appreciably different from each other, two of the four stretching vibrations of the PdO_4 fragment would be better described as predominantly Pd–O_m stretches, the remaining two being mostly Pd–O_b in character. The former pair would have higher frequencies than the latter, the frequency difference *whithin each pair* being difficult to estimate *a priori*.

The infrared spectrum of the crystals isolated from the solutions in glacial acetic acid in which negatively charged complexes were shown to be formed is given in Fig. 6. Although the spectrum is certainly not of the desired high quality, it is not inconsistent with the proposed structure. That is, as can be seen, in the region where the Pd–O bands are expected to appear, at least two bands could be attributed to palladium-oxygen stretches. The first of these is the band appearing around 450 cm^{-1}, the other one lying below 300 cm^{-1}. If this assignment is correct,

then the frequency difference is in agreement with the expectations outlined above. It should be noted that the frequency of the 450 cm^{-1} band is comparable to that of the corresponding band in the spectrum of palladium acetylacetonate (464 cm^{-1}) [22, 23] and appreciably higher than that in the trimeric palladium acetate (378 cm^{-1}) [24], implying the presence of stronger Pd–O bonds than in $2[Pd_3(CH_3COO)_6] \cdot H_2O$.

The spectral picture in the region of the carboxylate stretching vibrations also fits the expectations. That is broad and intense bands are, found around 1685 and 1290 cm^{-1} and they can be attributed to the carboxylate stretching vibrations of the monodentate acetates, the former frequency being *higher* and the latter *lower* than in the spectrum of the trimeric palladium(II) acetate [24]. On the other hand, additional bands are present at intermediate frequencies and these bands can be attributed to the vibrations of the carboxylate groups of the bridging acetates (and/or to the methyl bending vibrations which are also expected to appear in this region).

Althought the assignments presented above should not be considered as indisputable, taken together with all other relevant data, they seem to show that the formula presented above is likely to reflect correctly the structure of the complex formed in acetic acid.

REFERENCES

[1] R.G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

[2] R. G. Pearson, *J. Chem. Educ.*, **45**, 581 (1968).

[3] R. G. Pearson, *J. Chem. Educ.*, **45**, 643 (1968).

[4] T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. R. Heffer and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

[5] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **29**, 2122 (1967).

[6] A. C. Skapski and M. L. Smart, *Chem. Commun.*, **1970**, 658.

[7] F. A. Cotton and S. Han, *Rev. Chim. Miner.*, **20**, 496 (1983).

[8] F. A. Cotton and S. Han, *Rev. Chim. Miner.*, **22**, 277 (1985).

[9] D. H. R. Barton, J. Khamsi, N. Ozbalik, M. Ramesh and J. C. Sarma, *Tetrahedron Lett.*, **30**, 4661 (1989).

[10] R. W. Brandon and D. W. Claridge, *Chem. Commun.*, **1968**, 677.

[11] R. N. Pandey and P. M. Henry, *Can. J. Chem.*, **52**, 1241 (1974).

[12] V. Vajgand, M. Jaredić, I. Spirevska, M. Milovanov and R. Džudović, *Lucralile Celei de a III-a conferinte nationale de chemie analitica*, **1**, 183 (1971).

[13] В. Вајганд и Л. Шоптрајанова, *IV советување на хемичарите и тсхнолозите на Македонија, III собир "Наука-стопанство"*, Секција хемија и технологија, стр. 28, Скопје, 1974.

[14] В. Вајганд и Л. Шоптрајанова, *V советување на хемичарите и технолозите на Македонија*, Синопсиси, стр. 45, Скопје, 1975.

[15] В. Вајганд и Л. Шоптрајанова, *Год. Зборник Хем. Фак., Унив. Скопје*, **27**, 17 (1977).

[16] Л. Шоптрајанова, *X советување на хемичарите и технолозите на Македонија*, Трудови, стр. XLVII, Скопје, 1987.

[17] D. H. Tempelton, G. W. Watt and C. S. Garner, *J. Amer. Chem. Soc.*, **65**, 1608 (1943).

[18] A. J. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1961.

[19] Г. Л. Шлефер, *Комплексообразование в растворах*, Химия, Москва, 1964.

[20] Б. И. Набиванец и Л. В. Калабина, *Ж. Неорг. Хим.*, **15**, 1595 (1970).

[21] G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, **33**, 227 (1980).

[22] H. Junge and H. Musso, *Spectrochim. Acta*, **24**A, 1291 (1968).

[23] K. Nakamoto, C. Udovich and J. Takemoto, *J. Amer. Chem. Soc.*, **92**, 3973 (1970).

[24] L. Šoptrajanova and B. Šoptrajanov, *Spectrosc. Lett.*, **25**, 1131 (1992).

Р е з и м е

ФОРМИРАЊЕ НА АЦЕТАТНИ КОМПЛЕКСИ НА ПАЛАДИУМ(II) ВО ВОДЕНА И ВО НЕВОДЕНА СРЕДИНА

Лидија Шоптрајанова и Илинка Спиревска

Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј", пошт. фах 162, 91001 Скопје, Македонија

Клучни зборови: Паладиум; ацетати; комплекси; глацијална киселина; потенциометрија.

Испитани се, во водена и во неводена средина, реакци-те на формирање ацетатни комплекси на паладиум(II). Забе-лежано е дека во водена средина се формираат ацетатни (или мешани) комплекси со просечен број лиганди близок до четири. Во глацијална оцетна киселина доаѓа до формирање на $Na_2[Pd_2(OAc)_6]$ кога кон паладиум(II) ацетат се додава натриум ацетат. Снимен е инфрацрвениот спектар на добие-ното комплексно соединение.

INTRODUCTION

EXPERIMENTAL