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Palladium(II) Complexes of Hydrazides of Aspartic and Glutamic Acids

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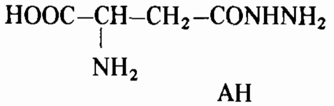
Two types of Pd(II) complexes (B and C) of hydrazides of aspartic and glutamic acids were synthesized and studied. The type B complexes are of the general formula $[Pd_2(LH)_2Cl_2]X_2$ *with two bridging chloride ions, where* $X = Cl^-$ *or* OH^- *depending on the pH value. The ligands are bonded through the amino carboxylic* NH_2 *group and the hydrazide oxygen, the carboxylic group being deprotonated and uncoordinated. In the type C complexes the ligands are bonded through a* NH_2 *group and the deprotonated hydrazide nitrogen. At M:L = 1:1 and pH ~2 the complexes again have the general content* $[Pd_2(LH)_2Cl_2]Cl_2$*, but with protonated carboxylic groups. At M:L = 1:2 two types of complexes C were synthesized, depending on the pH of the solution. At pH 2.50 mononuclear ionic complexes* $[Pd(LH)_2]Cl_2$ *are formed, with protonated carboxylic groups of the ligands, while at pH 3.50 the neutral species* PdL_2 *are obtained with deprotonated carboxylic groups.*

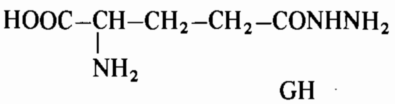
Introduction

Recently we have obtained and studied the complexes of copper(II), nickel(II) and cobalt(II) with the hydrazides of aspartic and glutamic acids [1, 2]. These ligands are of interest with respect of the several donor atoms serving as potential sites for coordination with metal ions, and also because of their physiological activity [3]. Taking into account the increased tendency for bonding with nitrogen and the cytostatic action of many coordination compounds of platinum metals, we began a series of experiments on the synthesis of palladium and platinum complexes of these hydrazides and to the investigation of their structure. The present paper presents the results for the palladium(II) complexes of β-hydrazide of aspartic acid (AH) and of γ-hydrazide of glutamic acid (GH):



$$\mathrm{HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}CONHNH_2}$$

AH



$$\mathrm{HOOC{-}\underset{\displaystyle NH_2}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}CONHNH_2}$$

GH

Experimental

The hydrazides AH and GH were synthesized and purified as described in the literature [4]. All other reagents used were of A.R. grade. Two types of complexes (B and C) with different content and structure were obtained. The complexes B were synthesized by mixing cooled aqueous solutions of K_2PdCl_4 and the corresponding ligand in 1:1 and 1:2 metal to ligand ratios. After several hours the precipitate formed was filtered and dried over NaOH. The complexes C were obtained from $PdCl_2$ dissolved in 0.1 *M* HCl + acetone (50% v/v) and from the ligand dissolved in water + acetone (50% v/v) with Pd:L ratio 1:1 and 1:2. The complexes were filtered and dried at low pressure over P_2O_5 at room temperature. If acetone is removed by heating the complexes change as follows from their IR spectra.

Both type B and C complexes can also be obtained in the corresponding conditions from $(NH_4)_2PdCl_6$ and the ligands, taken in a sufficient amount for reduction of Pd(IV) to Pd(II) and for coordination of the last species. In this case part of the ligand is oxidized to acid (aspartic or glutamic), but nevertheless Pd(II) forms complexes only with the hydrazides present in excess. The oxidation state +2 for palladium in these complexes was proved by the ESCA method. Thus for the type C complexes obtained with $(NH_4)_2PdCl_6$ the following values were found for the energy of electron detachment from Pd $3d_{5/2}$ level: with Pd:AH = 1:5 it is 338.6 eV, with Pd:GH = 1:5 it is 338.9 eV, indicating definitely the Pd(II) oxidation state [5].

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The elemental analysis was performed according to standard procedures. Nitrogen was determined by the Duma method, the total chlorine assay after destruction of the complexes (melting with Na_2CO_3) was determined both titrimetrically and gravimetrically as AgCl. The ionic chloride was titrated potentiometrically with $AgNO_3$. Palladium was determined gravimetrically with dimethylglyoxime.

The electronic spectra in solutions were recorded on a Specord UV–VIS spectrophotometer and the reflectance spectra on a VSU 2P spectrophotometer (Carl Zeiss). The IR spectra were obtained on a Perkin-Elmer model 580 spectrophotometer in KBr pellets and the DTA data with a microdifferential thermoanalyser MIKRO ATD M4. The ESCA measurements were carried out on a VIEE-15 spectrometer and the carbon 1s photoelectron line (285.0 eV) was used for energy calibration.

Results

Complexes of Type B

The complexes with AH and GH were obtained from systems with M:L = 1:1 and 1:2 as light yellow precipitates. The pH of the solution over the precipitate in a system with M:L = 1:1 is 3.7–4.0 and with M:L = 1:2 it is higher (pH ~ 5). The solid substances obtained from solutions with M:L = 1:1 represent ionic salts of the type $[Pd_2(LH)_2Cl_2]Cl_2 \cdot 3H_2O$. The crystalohydrate water was determined by DTA at ~ 125 °C.

The precipitates obtained from systems with M:L = 1:2 do not contain ionic chloride, which in this case seems to be substituted by OH^- to $[Pd_2(LH)_2Cl_2](OH)_2$. These complexes do not contain crystalohydrate water removed at relatively low temperature and water from OH^- was determined at higher temperature (~ 160 °C).

The results for the elemental analysis data are summarized in Table I.

The titration curves of the complexes $[Pd_2(LH)_2Cl_2]Cl_2$ show that the complexes contain two acidic groups which can be titrated with NaOH (Fig. 1a). Taking into account the pH value at the equivalence point it seems that the protonated aminogroup of the hydrazide, $-CONH\overset{+}{N}H_3$, is titrated.

The titration of the 1:2 complexes with $HClO_4$ has shown that they contain two proton-acceptor groups, which is in accordance with the formula

TABLE I. Elemental Analysis Data.

M:L Ratio in the Soln.	Complex Formed	Found (Calcd.) %				
		Pd	Cl	N	C	H_2O
Complexes of type B						
1:1	$[Pd_2(AH)_2Cl_2]Cl_2 \cdot 3H_2O$	30.43 (30.27)	20.08 (20.17)	12.37 (11.96)	13.72 (13.67)	7.10 (7.69)
1:2	$[Pd_2(AH)_2Cl_2](OH)_2$	34.93 (34.77)	11.93 (11.59)	13.98 (13.74)	15.78 (15.70)	–
1:1	$[Pd_2(GH)_2Cl_2]Cl_2 \cdot 3H_2O$	29.36 (29.11)	19.17 (19.40)	11.32 (11.50)	16.58 (16.43)	6.92 (7.40)
1:2	$[Pd_2(GH)_2Cl_2](OH)_2$	33.50 (33.25)	10.85 (11.08)	12.79 (13.13)	19.08 (18.76)	–
Complexes of type C						
1:1	$[Pd_2(AH)_2Cl_2]Cl_2$	32.88 (32.80)	21.76 (21.85)	12.68 (12.96)	14.74 (14.81)	–
1:2	$[Pd(AH)_2]Cl_2$	22.33 (22.56)	15.19 (15.04)	17.96 (17.83)	20.52 (20.37)	–
1:2	PdA_2	26.58 (26.69)	–	20.82 (21.09)	23.84 (24.10)	–
1:1	$[Pd_2(GH)_2Cl_2]Cl_2$	31.12 (31.44)	20.68 (20.95)	12.24 (12.42)	17.68 (17.74)	–
1:2	$[Pd(GH)_2]Cl_2$	21.12 (21.30)	14.42 (14.19)	17.04 (16.82)	24.12 (24.04)	–
1:2	PdG_2	25.08 (24.95)	–	19.48 (19.71)	27.88 (28.16)	–

TABLE II. Infrared Spectral Bands (cm^{-1}).

Free Ligands	Complexes of Type B	Complexes of Type C	Assignment
3460 br*	3460 br*	3440 br*	ν(NH) and/or ν(OH) uncoord. NH_2 resp. $\overset{+}{N}H_3$ and/or water resp. OH^-
–	–	$1720^{a,b}$	ν(C=O) from –COOH
1650–1670	1650–1670	$1650–1670^{c}$	$\nu(COO^-)_{asym.}$
1610–1630	1620–1640	1620	amide (I)
1535–1550	1540–1560	–	amide (II)
1510	1510	1510	$\delta(\overset{+}{N}H_3)$
1400	1400	1400^{c}	$\nu(COO^-)_{sym.}$
–	–	1375	ν(C–N) in a chelate ring through nitrogen
1310	1340	–	amide (III)
1020	1090	1080	ν(N–N)
–	530–540	530–550	$\nu(Pd–NH_2)$
–	–	405 + 385	ν(Pd–N) from the hydrazide group
–	330 + 340 280 – 300 250 – 260	330 + 340 280 – 300 250 – 260 ^{a} – ^{b,c}	ν(Pd–Cl)

*Broad band. [a]In complexes obtained from solutions with M:L = 1:1. [b]In complexes obtained when M:L = 1:2 and pH 2.50. [c]When M:L = 1:2 and pH 3.50.

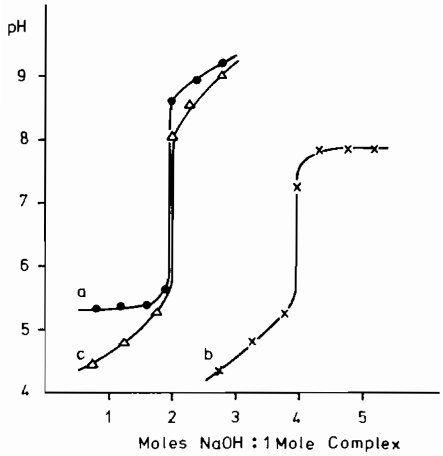


Fig. 1. Titration of complexes with 0.1 *M* NaOH. a) Titration curve for the type B complex $[Pd_2(GH)_2Cl_2]Cl_2$; titration curves for the type C complexes: b) for $[Pd(GH)_2]Cl_2$, c) for PdG_2.

$[Pd_2(LH)_2Cl_2](OH)_2$. After the titration the complexes $[Pd_2(LH)_2Cl_2](ClO_4)_2$ were obtained from the solution.

The IR data (Table II) have shown that the carboxylic group both in the free ligands and in the complexes is deprotonated and does not participate in coordination [$\nu(COO^-)_{asym}$ = 1650–1670 cm^{-1}, $\nu(COO^-)_{sym}$ = 1400 cm^{-1}]. Amide (I) in the ligands appears at 1610–1620 cm^{-1} but it is difficult to determine the exact position of this band in the complexes due to the δ(H–O–H) vibrations of water. Amide (II) is slightly shifted from 1535–1550 cm^{-1} in the ligands to 1540–1560 cm^{-1} in the complexes, while amide (III) moves from 1310 cm^{-1} to 1340 cm^{-1}. These data indicate that most probably the hydrazide group is coordinated to palladium via oxygen and not through nitrogen [6, 7]. The bonding of the hydrazide group to palladium might be responsible also for the shift of the ν(N–N) from 1020 cm^{-1} in the ligands to 1090 cm^{-1} in the complexes.

The band at ~1500 cm^{-1} in the ligands and in the complexes is assigned to the presence of protonated amino group $\overset{+}{N}H_3–\overset{|}{C}H–COO^-$ in the ligands and of $–CONH\overset{+}{N}H_3$ in the complexes. The coordination of NH_2 from the aminocarboxylic group follows from the shift of 3280–3290 cm^{-1} band in the free ligands to 3180–3200 cm^{-1} in the complexes. This is also confirmed by the appearance of ν(Pd–N) at 530–540 cm^{-1} [8]. The intense broad band at 3450–3460 cm^{-1} can be assigned to the uncoordinated protonated hydrazide group $–CONH\overset{+}{N}H_3$ [9] and/or to the presence of water of OH^- in the complexes.

The bands at 250–260 cm^{-1}, 280–300 cm^{-1} and the intense doublet at 330 + 340 cm^{-1} are a sure sign for the chloride ions present as bridging ligands [8, 10]. The assignment of these bands was confirmed also by the spectra of the same type complexes obtained with water solutions of $Pd(NO_3)_2$ instead of K_2PdCl_4, in which these bands disappear.

The electronic reflectance spectra of the complexes of type B do not show absorption bands in the visible range, the strong band at 465 nm and the less intense one at 429 nm in the spectra of K_2PdCl_4 being substituted only by a broad shoulder at ~370 nm in the complexes $[Pd_2(LH)_2Cl_2]Cl_2$, shifted to ~350–360 nm in the complexes $[Pd_2(LH)_2Cl_2](OH)_2$.

According to the literature data [11] the initial solutions of Pd(II) we have used contain palladium chloride dimeric species from which complexes of the type $[Pd_2(LH)_2Cl_2]^{2+}$ could be easily obtained. On the other hand the relatively high frequencies of the bands obtained preclude the presence of the complexes $[PdCl_4]^{2-}$ or $[Pd_2Cl_6]^{2-}$ in the solid substances [12] or the formation of mononuclear palladium complexes with the ligands studied [13]. The position of the d–d band at 350–370 nm is indicative for the square planar arrangement of the ligands around the metal [14].

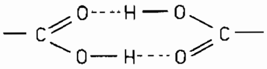
The oxidation state Pd(II) in the type B complexes was proved by the ESCA method, giving the following bonding energies of the Pd $3d_{5/2}$ level: for $[Pd_2(AH)_2Cl_2](OH)_2$ it is 338.5 eV and for $[Pd_2(GH)_2Cl_2](OH)_2$ 338.6 eV, values typical for Pd(II) compounds [5].

Complexes of Type C

These complexes represent yellow to orange substances obtained from solutions with M:L = 1:1 at pH ~ 2 and with 1:2 ratio at pH 2.50 and 3.50. The first complexes are again ionic chloride salts with the same content $[Pd_2(LH)_2Cl_2]Cl_2$ (Table I) as the corresponding complexes of type B, except for the crystalohydrate water, but with different structure as follows from their IR spectra. The complexes of the type C obtained from solutions with M:L = 1:2 are of two types, depending on the pH values of the solutions, after mixing the reagents (Table I). The complexes obtained at pH 2.50 are of the general formula $[Pd(LH)_2]Cl_2$ and those formed at pH 3.50 are neutral mononuclear species PdL_2.

The titration of the complexes isolated as solid substances from solutions with M:L = 1:2 and pH 2.50 have shown that two protons are titrated in every coordinated ligand (Fig. 1b), being most probably the protons of carboxylic and protonated hydrazide groups. The titration curves for the complexes obtained from solutions with M:L = 1:2 and pH 3.50 revealed that here only one acidic group—the protonated $\overset{+}{N}H_3$ from the hydrazide group—is titrated in every ligand (Fig. 1c). The type C complexes obtained from solutions with M:L = 1:1 could not be titrated with NaOH because at pH > 2.7 evolution of N_2 was observed, together with reduction of Pd(II) to black elemental palladium.

The IR data for the complexes C indicate a significant structural difference from the complexes B. The carboxylic groups of the ligands in the complexes C with M:L = 1:1 (the last being obtained at pH 2.50) are protonated and are not involved in coordination as follows from the band at 1720 cm^{-1}. The COOH groups both in the ligands and in these complexes are engaged in H-bond formation, as evident from the set of bands at ~3000 cm^{-1}, 2650 cm^{-1}, 1420 cm^{-1}, 1285 cm^{-1} and 935 cm^{-1} [15], typical for dimers of the type:



In the IR spectra of the complexes obtained from solutions with M:L = 1:2 and pH 3.50 the band for COOH at 1720 cm^{-1} is substituted by the bands at 1660 and 1400 cm^{-1}, corresponding to the deprotonated and non-coordinated COO^- group.

The most interesting difference in the IR spectra is connected with the coordination of the hydrazide group. Here the ν(C=O) mode is seen as very strong and sharp band at 1620 cm^{-1}, while amide (II) and amide (III) bands connected with N–H vibrations in the amide group disappear. Instead a new intense and sharp band is observed at 1375 cm^{-1}. Such a band is usually present in palladium complexes where a deprotonated amide group from hydrazides or peptides is included in a chelate ring with the metal ion and it is usually assigned to ν(C–N) mode [16, 17]. The formation of a direct Pd–N bond through the deprotonated amide nitrogen is also confirmed by the appearance of a new doublet at 385 + 405 cm^{-1} which is characteristic for ν(M–N) in hydrazide complexes [18]. The presence of a band at 530–540 cm^{-1} shows that NH_2 from the aminocarboxylic group is still bonded to the metal. This is also confirmed by the shift of the 3280–3290 cm^{-1} band in the free ligands to 3150–3170 cm^{-1} in the corresponding complexes.

The electronic spectra have shown that when a ligand solution is added to a solution of $PdCl_2$ in 0.1 *M* HCl + acetone the absorption band at 472 nm due to the dimeric form $Pd_2Cl_6^{2-}$ is shifted to shorter wavelengths (Fig. 2). The spectra were recorded after removal of acetone under vacuum and filtration of the precipitate, which at M:L = 1:1 represents $[Pd_2(LH)_2Cl_2]Cl_2$ and at M:L = 1:2 it is $[Pd(LH)_2]Cl_2$.

The absorption maximum at 408 nm in the last case, which in the presence of acetone shifts to 400 nm, strongly supports the assumption that square planar mononuclear $Pd(LH)_2^{2+}$ is formed [13]. The same is valid also for the reflectance spectra of the complexes $[Pd(AH)_2]Cl_2$ and $[Pd(GH)_2]Cl_2$, shown on Fig. 3.

The ESCA data obtained for the type C complexes proved that the metal is present as Pd(II). The measured binding energies of the Pd $3d_{5/2}$ level are 338.9

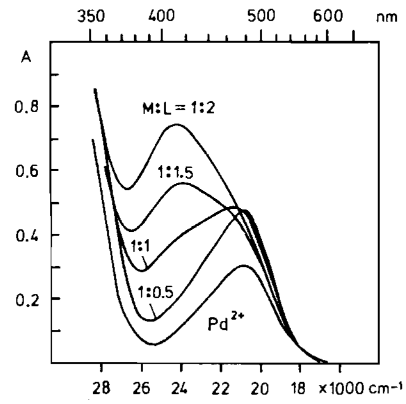


Fig. 2. Electronic spectra of the type C complex $[Pd(AH)_2]Cl_2$, formed in solution with different M:L ratio and pH 2.50. The total solution volume (10.0 ml) and Pd(II) concentration ($C_{Pd^{2+}}$ = 0.01 *M*) are constant in all samples. A 0.5 cm pathlength cell was used for the solutions of the complex and 0.1 cm cell for the solution of Pd(II).

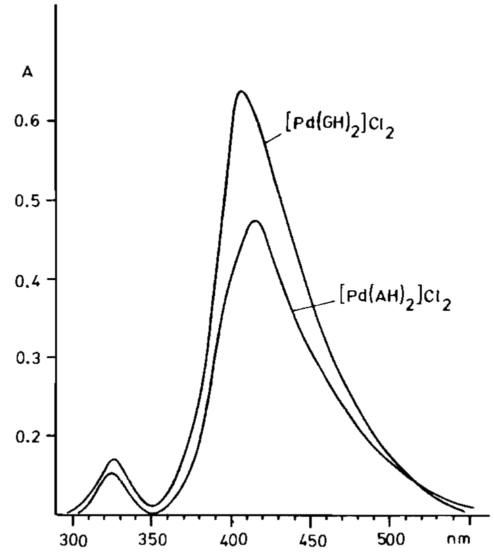


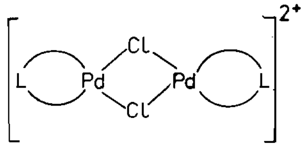
Fig. 3. Electronic reflectance spectra of the type C complexes $[Pd(AH)_2]Cl_2$ and $[Pd(GH)_2]Cl_2$.

and 338.6 eV for $[Pd(AH)_2]Cl_2$ and $[Pd(GH)_2]Cl_2$ respectively, which are normal for Pd(II) compounds [5].

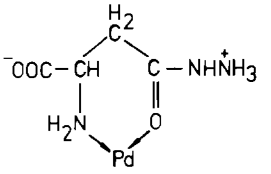
Discussion

Complexes of Type B

The experimental data for the complexes B are consistent with the following structures of the complex ion with Cl^- or OH^- as counter-ions, when the M:L ratio in the system is 1:1 (pH 3.7–4.0) or 1:2 (pH ~ 5) respectively. This structure is supported by the elemental analysis, by the presence of two



coordinated chloride ions in a *cis* bridging position, according to the IR data, and by the positive sign of the complex as well. The bonding of the ligand AH with a formal neutral change in these conditions can be represented as follows



Structure I

The IR data obtained also definitely support structure I, namely the data for the presence of nonbonded $-COO^-$ and hydrazide nitrogens, together with the indications for bonding of NH_2 and the hydrazide carbonyl oxygen. The presence of deprotonated carboxylate in this pH range is also confirmed by the available pK_a data for –COOH in the aminocarboxylic group of aspartic and glutamic acids [19].

The coordination of palladium through C=O and not through the hydrazide nitrogen is realized here, because it is well known [20] that compounds with –CONH– group coordinate metal ions through nitrogen only if deprotonation of the amide nitrogen takes place as, for example, is the case with complexes of type C. If such deprotonation does not happen, the trigonal hybridization sp^2 will change to a tetrahedral one and the resonance in the amide group would be lost [20]. An important role for this type of bonding seems also to be played by the bridging chloride. The presence of the hard ligand Cl^- makes Pd(II) harder and thus increases its ability for coordination both with the aminocarboxylic NH_2 and with the hydrazide C=O [21]. On the other hand simultaneous chelation by the three donor groups $-NH_2$, $-COO^-$ and –CONH– is impossible at least for Pd(II) [22].

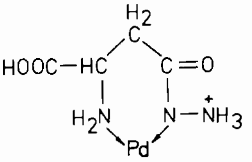
The type B complexes of GH with structure I should contain a seven membered chelate ring. Nevertheless the formation of such complexes is possible, due to the high value of CFSE for the complexes of Pd(II), Pt(II) and Cu(II) with nitrogen-containing donors which can stabilize even seven-membered rings [20, 22].

The idea for the type B complexes structure discussed here is confirmed also by the fact that at pH > 9 the protonated hydrazide groups in the complexes are neutralized, the complex $[Pd_2(LH)_2Cl_2]^{2+}$ becomes neutral and can be extracted by $CHCl_3$.

As to the crystalohydrate water, in some other cases of palladium(II) complexes with protonated amides [7, 17] crystalohydrates with two or three water molecules have been obtained.

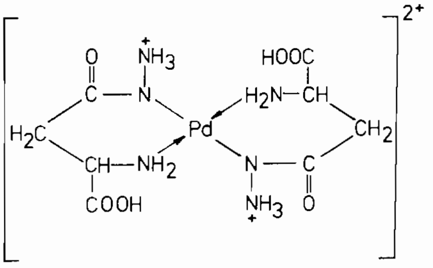
Complexes of Type C

All the experimental data for the complexes type C show that in this case the ligands are bonded to palladium through NH_2 from the aminocarboxylic group and through the deprotonated hydrazide nitrogen.



Structure II

In the type C complexes obtained from systems with M:L = 1:1 and pH ~ 2 the complexes have the same general formula $[Pd_2(LH)_2Cl_2]Cl_2$ as the corresponding type B complexes with two bridging and two ionic chlorides. In the presence of larger amounts of the ligand (M:L = 1:2) the chloride bridges are broken and Cl^- is substituted completely by the ligand, with the formation at pH 2.50 of mononuclear complex species.



When the complexes are formed at higher pH values (pH 3.50) the carboxylic groups of the ligands are deprotonated and the neutral species PdL_2 formed.

Metal ions such as Cu(II), Zn(II), Ni(II), Co(II), Co(III), Fe(III) form complexes with ligands containing –CONH– group through deprotonation of the amide nitrogen in the pH range 4–10 [7, 23]. Platinum(II), and especially palladium(II), are the most suitable metal ions for coordination through the deprotonated amide nitrogen [16, 17, 20, 22], due to their affinity for coordination with nitrogen. For this reason Pd(II) and Pt(II) form complexes of that type at very low pH values (pH ~ 2) when even the carboxylic groups of the ligands are still protonated [20, 24].

It must be emphasized that the IR spectra of the 1:1 type B complexes, obtained after removal of the crystalohydrate water at 125 °C, have shown that although their content in this case is the same as that of the 1:1 type C complexes, they differ markedly in several points. Thus, the amide (II) and amide (III) bands in the spectra of type B disappear in the spectra of type C. On the other hand, the typical bands for type C at 1375 cm^{-1} and the doublet at 405 + 385 cm^{-1} are not observed in the type B spectra. These facts confirm again that even when the type B and C complexes have the same general content, they differ in structure.

The role of acetone in the process of formation of the type C complexes obtained is probably connected with its ability to solvate palladium(II) [12] and thus to help the substitution of Cl^- by the ligands. Additional support to this idea is given by the fact that in acetone solutions the splitting of the halogen bridges in $Pd_2Cl_6^{2-}$ proceeds easily and in the presence of ligands formation of mononuclear palladium(II) complex species is observed [25]. It can thus be explained why it is possible to obtain the mononuclear complexes PdA_2 and PdG_2 starting either from $PdCl_4^{2-}$ in 50% acetone or from acetone solution of $PdCl_2$, while in the absence of chloride PdA_2 and PdG_2 can be obtained from water solutions of $Pd(NO_3)_2$.

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