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Synthesis, structure, and hydrolytic reaction of *trans*-dichlorobis(diethanolamine-*N*)palladium(II) with *N*-acetylated *L*-histidylglycine dipeptide

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Abstract

The reaction of $PdCl_2$, or K_2PdCl_4, with diethanolamine (DEA), in the molar ratio 1:2, affords the *trans*-$[PdCl_2(DEA)_2]$ complex. X-ray structure analysis of this complex confirmed the formation of the *trans*-isomer. The complex crystallizes in the space group $P4_2bc$. The central Pd(II) ion is coordinated in an almost ideal square-planar fashion with a small deformation of the Cl–Pd–Cl angle (175.6(7)°) due to N–H···Cl hydrogen bonding. The N–H group participates in a bifurcated interaction with the two symmetry related Cl^- anions. The hydroxyl groups of the diethanolamine ligand form very strong hydrogen bonds between the complex units, thus leading to infinite zigzag (O–H···O–H···O–H ··) chains in the crystal packing. The complex units are further connected by weaker intermolecular hydrogen bonds of the N–H···Cl type in a way to form layers parallel to the crystallographic (001) plane. The reaction between the *trans*-$[PdCl_2(DEA)_2]$ or *trans*-$[Pd(H_2O)_2(DEA)_2]^{2+}$ complex and MeCOHis-Gly dipeptide at $1.5 < pH < 2.0$ and at 25 °C leads to the regioselective cleavage of the amide bond involving the carboxylic group of the histidine. The cleavage of the substrate was fast and went almost to completion within less than one hour.

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1. Introduction

Recent years have witnessed increasing interest in the study of the interactions of platinum(II) and palladium(II) complexes with sulfur- and histidine-containing peptides and proteins [1–4]. Interest in the study of these interactions also became of capital importance after the discovery that platinum(II) [5] and palladium(II) [6–13] aqua complexes can be promising reagents for the hydrolytic cleavage of the above mentioned peptides. In generally, it was shown that platinum(II) and palladium(II) aqua complexes bind to the heteroatom in the side chain of methionine [5–9] or histidine [10–13] and promote cleavage of the amide bond involving the carboxylic group of this anchoring amino acid. During the last ten years, hydrolytic reactions between various palladium(II) complexes of the type *cis*-$[Pd(L)(H_2O)_2]^{2+}$, in which L is a bidentate coordinating ligand, and sulfur- and histidine-containing peptides have been extensively investigated [10–17]. The *cis* configuration of two water molecules and a very stable chelating diamine ligand (L) in *cis*-$[Pd(L)(H_2O)_2]^{2+}$ complexes have been shown to be very suitable for the study of the mechanism of these regioselective hydrolytic reactions. In spite of the numerous results obtained recently, the very complicated mechanism of these hydrolytic reactions is yet to be completely understood. For the clarification of this mechanism, it was shown to be necessary to investigate these regioselective cleavage reactions with structurally different palladium(II) complexes. In the present study, a new palladium(II) complex, *trans*-$[PdCl_2(DEA)_2]$ (DEA = diethanolamine), was synthesized and employed to study its hydrolytic activity in its reaction with *N*-acetylated *L*-histidylglycine dipeptide. The obtained results of an ^{1}H NMR study of the regioselective hydrolytic cleavage of the amide bond in *N*-acetylated *L*-histidylglycine in its reaction with *trans*-$[PdCl_2(DEA)_2]$ and *trans*- $[Pd(H_2O)_2(DEA)_2]^{2+}$ complexes, both containing two monodentate coordinated DEA ligands in the *trans*-position, are promising and may help in the development of new palladium(II) complexes as artificial metallopeptidases.

2. Materials and methods

Distilled water was demineralized and purified to a resistance greater than 10 MΩ cm. The compounds D_2O, DNO_3, NaOD, $K_2[PdCl_4]$, $PdCl_2$, and diethanolamine (DEA; $NH(CH_2CH_2OH)_2$) were obtained from Aldrich Chemical Co. All common chemicals were of reagent grade. The dipeptide *L*-histidylglycine (His-Gly) was obtained from the Sigma Chemical Co. The terminal amino group in His-Gly was acetylated by standard methods to obtain MeCOHis-Gly [6].

All *pH* measurements were made at 25 °C using an Iskra MA 5704 *pH* meter calibrated with Fischer certified buffer solutions of pH 4.00 and 7.00. The results were not corrected for the deuterium isotope effect. Reactions of MeCOHis-Gly with palladium(II) complex in D_2O solutions were followed by ^{1}H NMR spectroscopy using a Varian 200 MHz spectrometer. Equimolar amounts of the palladium(II) complex and the dipeptide were mixed in an NMR tube. The final solution was 20 mM in each reactant. The pH was varied in the range of $1.5 < pH < 2.0$. All reactions were carried out at 25 °C. The internal reference was

TSP (sodium trimethylsilylpropane-3-sulfonate). The UV-Vis spectra were recorded on a Perkin-Elmer Lamda 35 spectrophotometer using approximately 10^{-3} M aqueous solutions. The IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer using the KBr pellet technique. Elemental microanalyses for carbon, hydrogen, and nitrogen were performed at the Faculty of Chemistry, Belgrade University.

2.1. Crystal structure determination of trans-[$PdCl_2(DEA)_2$]

A yellow block-shaped single crystal of approximate $0.20 \times 0.12 \times 0.08$ mm size was covered with protective perfluoropolyalkylether oil. Data were collected at 100 K on a Bruker-Nonius KappaCCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on multiple scans was applied (SADABS [25], $T_{min} = 0.703$, $T_{max} = 0.870$). Crystal data: $C_8H_{22}Cl_2N\ {}_2O_4Pd$, ($M_r =$ 387.58), tetragonal, space group $P4_2bc$ (No. 106), $a = 9.835(1)$, $c = 14.328(2)$ Å, $V = 1385.9(3)$Å^3, $Z = 4$, $D_{calc} = 1.858$ g cm^{-3}, $\mu = 1.729$ mm^{-1}, $F(000) = 784$; 20852 reflections collected ($8.1° \leqslant 2\theta \leqslant 57.4°$), 1792 unique reflections, 1524 observed reflections [$I > 2\sigma(I)$]. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELXTL NT 6.12). All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were located in a difference Fourier synthesis and refined with a fixed common isotropic displacement parameter. Final residual indices: $R_1 = 0.0198$ [$I > 2\sigma(I)$], $wR_2 = 0.0451$ (all data), $GooF = 1.016$, absolute structure parameter = 0.09(5) [18], $\Delta\rho_{max} = 0.433$, $\Delta\rho_{min} = -0.359$ e · Å^{-3}.

3. Synthesis of the *trans*-dichlorobis(diethanolamine-*N*)palladium(II) complex, *trans*-[$PdCl_2(DEA)_2$]

3.1. Synthesis of the trans-[$PdCl_2(DEA)_2$] complex from $PdCl_2$

The complex *trans*-[$PdCl_2(DEA)_2$] was synthesized starting from $PdCl_2$ and diethanolamine in a molar ratio of 1:2. In the course of 3 h, the reaction of 0.18 g (0.001 mol) of $PdCl_2$ dissolved in 15 cm^3 of water with 0.21 g (0.002 mol) of diethanolamine, at 50–60 °C, afforded an orange solution which was left at room temperature for two days. The precipitated yellow-orange crystals were filtered off, washed with ethanol and air-dried. Yield 0.37 g (95%). Calculated for *trans*-[$PdCl_2(DEA)_2$] = $C_8H_{22}Cl_2N_2O_4Pd$ ($FW = 387.58$): C, 24.77; N, 7.22; H, 5.68%; found: C, 24.93; N, 7.20; H, 5.65%.

3.2. Synthesis of the trans-[$PdCl_2(DEA)_2$] complex from K_2PdCl_4

The *trans*-[$PdCl_2(DEA)_2$] complex was synthesized starting from K_2PdCl_4, according to a modified procedure published in the literature for similar Pt(II) complexes [18]. To K_2PdCl_4 (0.326 g, 0.001 mol) dissolved in 10 cm^3 of water was added 0.210 g (0.002 mol) of diethanolamine. The mixture was stirred at 60 °C for 1 h and 1 M HNO_3 was added slowly to the solution to maintain the pH at ~4.0. The resulting orange solution was left at room temperature for two days. The obtained yellow-orange crystals were filtered off, washed with ethanol and air-dried. Yield 0.27 g (70%). Calculated for

trans-[$PdCl_2(DEA)_2$] = $C_8H_{22}Cl_2N_2O_4Pd$ ($FW = 387.58$): C, 24.77; N, 7.22; H, 5.68; found: C, 24.85; N, 7.18; H, 5.55%.

Spectral characterization of the *trans*-[$PdCl_2(DEA)_2$] complex: ^{1}H NMR (200 MHz, D_2O): $\delta = 3.20$ (4H, -CH_2-NH, t, $J = 5.2$ Hz), 3.80 (4H, -CH_2-OH, t, $J = 5.2$ Hz) ppm; IR (KBr): $v = 466$, 488, 713, 1000–1070, 1185–1245, 3280–3380, 3374 cm^{-1}; UV-Vis (H_2O, 10^{-3} mol/dm^3): $\lambda_{max} = 384.38$ nm.

3.3. Synthesis of the trans-$[Pd(H_2O)_2(DEA)_2]^{2+}$ complex

This complex was prepared in the same manner as described in the literature for the preparation of aqua complexes from corresponding chloro complexes of Pt(II) and Pd(II) [19,20] The *trans*-[$PdCl_2(DEA)_2$] complex was treated in D_2O solution with the appropriate amount of $AgNO_3$. The Pd(II) complex and $AgNO_3$ were mixed in a molar ratio of 1:1.95 in order to avoid an excess of Ag^+ ions in the final solution of the aqua complex. The mixture was stirred at room temperature in the dark for up to 24 h. The precipitate of AgCl was removed and the filtrate containing the *trans*- $[Pd(H_2O)_2(DEA)_2]^{2+}$ was stored in a refrigerator until used further for reaction with the dipeptide.

4. Results and discussion

4.1. Crystal structure of the trans-$[PdCl_2(DEA)_2]$ complex

The *trans*-[$PdCl_2(DEA)_2$] complex (DEA = diethanolamine; $NH(CH_2CH_2OH)_2$) crystallizes in the space group $P4_2bc$ and its molecular structure is shown in Fig. 1. The coordination sphere of the central Pd(II) ion is comprised by two nitrogen donor atoms (from two DEA ligands) *trans* to each other and two chloro ligands again being in the *trans* position. The molecule itself is located on a crystallographic twofold axis parallel to the *z*-direction and exhibits therefore C_2 symmetry. The geometry of the complex is almost ideally

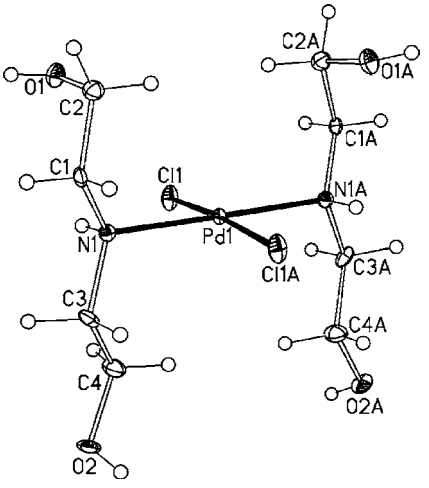

Fig. 1. Thermal ellipsoid plot of the *trans*-[$PdCl_2(DEA)_2$] complex (^{A} stands for the symmetry operation $-x + 1$, $-y + 1$, z).

square-planar with a displacement of the Pd(II) atom by 0.038(3) Å out of the mean N(1)N(1A)Cl(1)Cl(1A) plane. The Pd–N (2.071(2) Å) and Pd–Cl (2.300(1) Å) bond lengths lie well within the range of distances reported previously for the complexes of Pd(II) with amines [21–23].

The *cis* angles at Pd(II) [N(1)–Pd(1)–Cl(1), 88.91(5)° and N(1)–Pd(1)–$Cl(1)^A$, 91.11(5)° where $A = -x + 1, -y + 1, z$)], as well as the *trans* angle [(N(1)–Pd(1)–$N(1)^A$, 179.3(2)°] are close to ideal values i.e. 90° and 180°, respectively, while the observed Cl(1)–Pd(1)–$Cl(1)^A$ angle of 175.64(7)° shows a deformation from 180°; see Table 1. This deformation can be traced back to the formation of N–H···Cl hydrogen bonds. The N–H group participates in a bifurcated interaction leading to both an *intra*molecular N–H···Cl and an *inter*molecular N–H···Cl interaction to a neighbored molecule. In the crystal structure of *trans*-[$PdCl_2(DEA)_2$], –OH groups from the diethanolamine are involved in very strong hydrogen bonding interactions between complex units, forming infinitive zigzag (O–H···O–H···O–H ··) chains parallel to the *x* and/or *y* direction; see Fig. 2 and Table 2.

Table 1
Selected bond distances [Å] and angles [deg] for *trans*-[$PdCl_2(DEA)_2$]

Pd(1)–N(1)[a]	2.0707(16)
Pd(1)–N(1)	2.0707(16)
Pd(1)–Cl(1)	2.3004(6)
Pd(1)–Cl(1)[a]	2.3004(5)
N(1)[a]–Pd(1)–N(1)	179.3(2)
N(1)[a]–Pd(1)–Cl(1)	91.11(5)
N(1)–Pd(1)-Cl(1)	88.91(5)
N(1)[a]–Pd(1)–Cl(1)[a]	88.91(5)
N(1)–Pd(1)-Cl(1)[a]	91.11(5)
Cl(1)–Pd(1)-Cl(1)[a]	175.64(7)

[a] $(-x + 1, -y + 1, z)$.

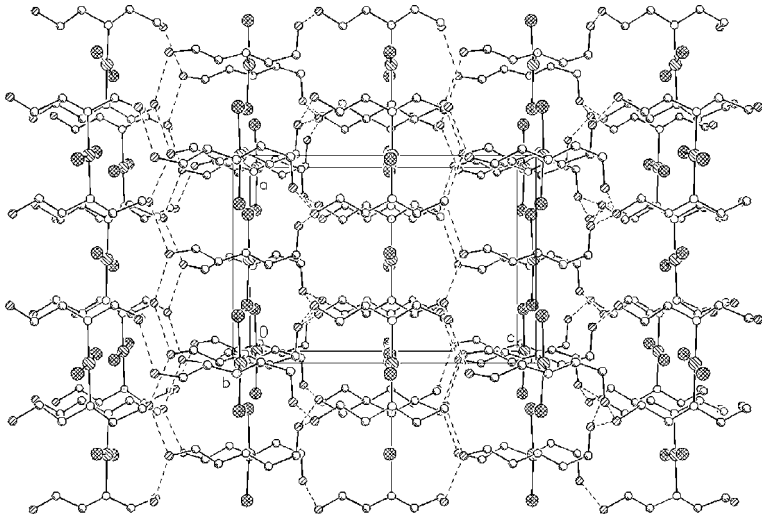

Fig. 2. Packing diagram showing the hydrogen bond network in the crystal structure of *trans*-[$PdCl_2(DEA)_2$].

Table 2
Selected hydrogen bonds for *trans*-[$PdCl_2(DEA)_2$] (Å and deg)

	D-H···A	D(D–H)	d(H···A)	D(D···A)	<(D–H···A)
A	N1–H1N···Cl1	0.84(3)	2.66(3)	3.066(2)	111(2)
B	N1–H1N···Cl1[a]	0.84(3)	2.91(3)	3.455(2)	124(2)
C	O1–H1O···O2[b]	0.77(3)	1.99(3)	2.723(3)	160(4)
D	O2–H2O···O1[c]	0.78(4)	2.03(4)	2.803(3)–	170(4)

[a] $x - 0.5, -y + 1.5, z$.
[b] $y - 0.5, x + 0.5, z + 0.5$.
[c] $-y + 1, x, z - 0.5$.

4.2. Hydrolytic reactions of *trans*-[$PdCl_2(DEA)_2$] and *trans*-[$Pd(H_2O)_2(DEA)_2$]$^{2+}$ complexes with MeCOHis-Gly

Hydrolytic reactions of *trans*-[$PdCl_2(DEA)_2$] and *trans*- [$Pd(H_2O)_2(DEA)_2$]$^{2+}$ complexes with *N*-acetylated *L*-histidylglycine dipeptide (MeCOHis-Gly) have been studied by ^{1}H NMR spectroscopy at $1.5 < pH < 2.0$ and at 25 °C. The corresponding palladium(II) complex and dipeptide were mixed in equimolar amounts with 20 mM total concentration of both reactants in D_2O solution. The reaction mixture was always kept acidic in order to suppress, or minimize, the dimerization that was reported to occur at $pH > 4.0$ [10–12,24]. However, in our case, an insoluble yellow product of an oligomeric hydroxo palladium(II)-dipeptide complex appeared at $pH > 2.0$.

The obtained results with either the *trans*-[$PdCl_2(DEA)_2$] or *trans*-[$Pd(H_2O)_2(DEA)_2$]$^{2+}$ complex and the MeCOHis-Gly dipeptide were compared with those for the reaction of this dipeptide and *cis*-[$Pd(en)(H_2O)_2$]$^{2+}$ (en is bidentate coordinated ethylenediamine ligand). Previous studies with the *cis*-[$Pd(en)(H_2O)_2$]$^{2+}$ complex and MeCOHis-Gly showed that five palladium(II)-peptide complexes are formed at $pH < 3.0$ [10–12,14,15]. These complexes were distinguished on the basis of the chemical shifts of the two imidazole protons, H-2 and H-5. The two major complexes were linkage isomers of each other with a unidentate coordination of palladium(II) *via* the N-3 or N-1 atom to the imidazole ring. The three minor complexes contained more than one palladium(II) atom per dipeptide, or involved more than one donor atom in the dipeptide. The experiments with MeCOHis-Gly selectively methylated at the N-1 or N-3 atom of imidazole and *cis*-[$Pd(en)(H_2O)_2$]$^{2+}$ showed that only palladium(II) with a monodentate coordination to the N-3 atom of imidazole can affect the cleavage of the amide bond involving the carboxylic group of histidine; none of the four other modes of coordination is effective [11]. The cleavage of the amide bond is regioselective and the reaction goes to completion in less than 72 h. Also, experiments with different histidine-containing peptides and different palladium(II) complexes showed that only unidentate coordination of the peptide via the N-3 atom of the imidazole to the Pd(II) ion affects hydrolytic cleavage of the amide bond. This was explained through the fact that this coordination mode permits the necessary close approach of the palladium(II) ion and of its aqua ligand to the scissile peptide bond [10,12,14–16].

In the reactions between the *trans*-[$PdCl_2(DEA)_2$] or the *trans*-[$Pd(H_2O)_2(DEA)_2$]$^{2+}$ complex with MeCOHis-Gly dipeptide, under the above mentioned conditions, five palladium(II)-peptide complexes were also observed. These complexes were distinguished on the basis of the chemical shifts of two imidazole protons, H-2 and H-5. These data were

compared with those obtained for the reaction of *cis*-$[Pd(en)(H_2O)_2]^{2+}$ and MeCOHis-Gly under the same experimental conditions. By comparison of these chemical shifts, it may be concluded that the palladium(II)-peptide complexes formed in the reaction of the *trans*-$[PdCl_2(DEA)_2]$ and *trans*-$[Pd(H_2O)_2(DEA)_2]^{2+}$ complex with MeCOHis-Gly are identical to those formed in the reaction of this dipeptide and the *cis*-$[Pd(en)(H_2O)_2]^{2+}$ complex [10–12,14,15]. In accordance with previous results for *cis*-$[Pd(en)(H_2O)_2]^{2+}$ with MeCO-His-Gly [11], it is assumed that only the palladium(II)-peptide complex with palladium(II) monodentately coordinated to the N-3 atom of imidazole is catalytically effective; see Fig. 3. In the reaction between the *trans*-$[PdCl_2(DEA)_2]$ or the *trans*-$[Pd(H_2O)_2(DEA)_2]^{2+}$ complex with MeCOHis-Gly dipeptide, free $DEAH^+$ ligand ($DEAH^+$ is protonated dieth-

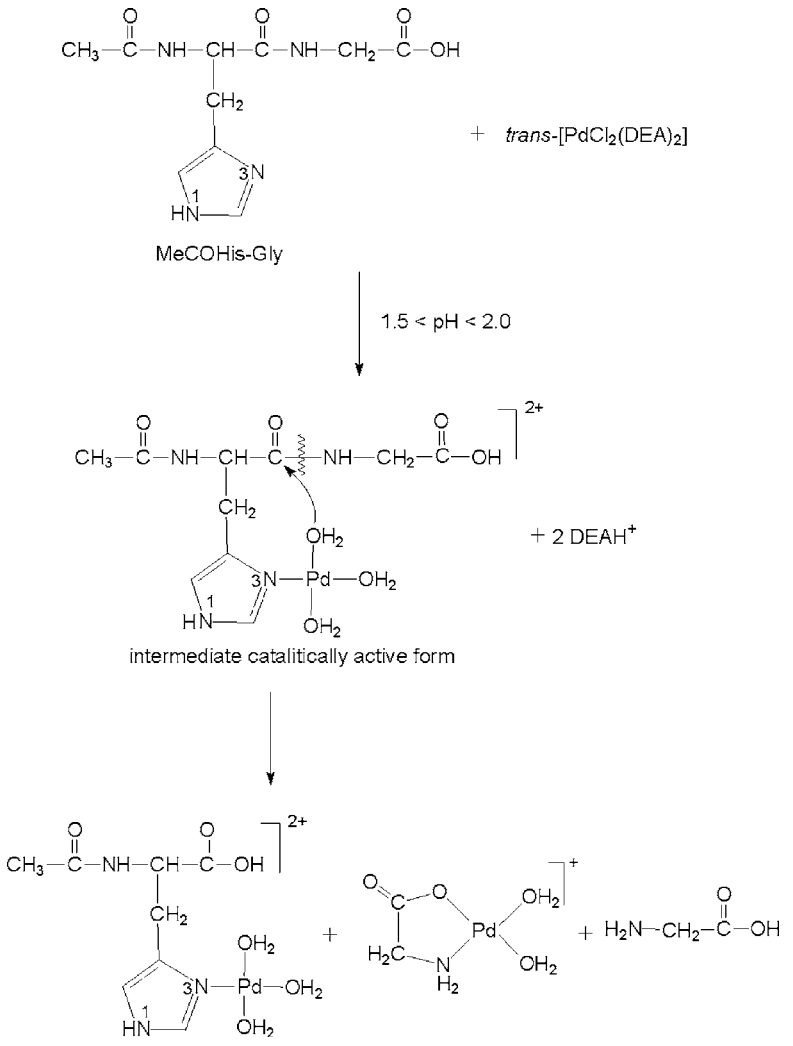

Fig. 3. Reaction pathway of *trans*-$[PdCl_2(DEA)_2]$ with MeCOHis-Gly at $1.5 < pH < 2.0$ and at 25 °C in water as solvent.

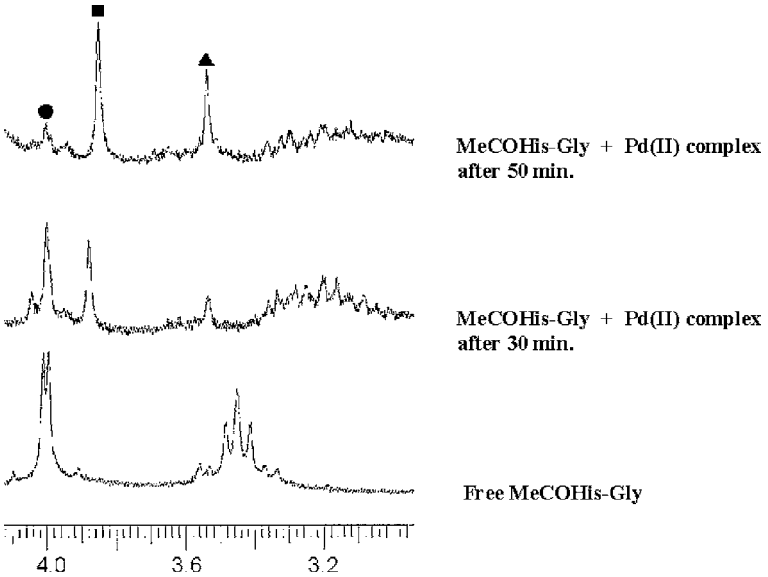

Fig. 4. Parts of ^{1}H NMR spectra for the hydrolytic reaction of MeCOHis-Gly with *trans*-$[PdCl_2(DEA)_2]$, or with *trans*- $[Pd(H_2O)_2(DEA)_2]^{2+}$, complex as function of time at $1.5 < pH < 2.0$ and at 25 °C in D_2O as solvent. The chemical shifts are in ppm relative to TSP. Resonances are indicated as follows: (●) methylene glycine protons of the none-hydrolyzed peptide; (■) methylene protons of free glycine; (▲) methylene glycine protons of the bis(bidentate) *cis*-$[Pd(Gly\text{-}N,O)(H_2O)_2]^+$ complex.

anolamine) can be detected in the ^{1}H NMR spectrum. Two triplets for the methylene protons of the free $DEAH^+$ ligand, 3.2 ppm for $–CH_2NH–$ and 3.8 ppm for $–CH_2OH$, appeared immediately in this spectrum. In all these reactions, only cleavage of the amide bond involving the carboxylic group of histidine was observed (Fig. 3). The cleavage of this amide bond was very fast and almost all the substrate was cleaved in less than 1 h. The selective cleavage of the dipeptide bond was observed by following the singlet at 3.96 ppm due to methylene glycine protons of the none-hydrolyzed substrate and the singlet at 3.86 ppm which corresponds to these protons in free glycine (Fig. 4). Addition of the amino acid glycine to the reaction mixture caused an increase of the signal at 3.86 ppm. In the reaction between the palladium(II) complex and MeCOHis-Gly, the resonance at 3.96 ppm in the dipeptide decreased, while that at 3.86 ppm for free glycine increased (Fig. 4). The concentrations of the dipeptide and the hydrolysis products were determined from the known initial concentration of MeCOHis-Gly and from the integrated resonance of the free glycine. Some of the liberated glycine reacts with the catalyst to form a small amount of the bis(bidentate) complex *cis*-$[Pd(Gly\text{-}N,O)(H_2O)_2]^+$, easily detected by ^{1}H NMR spectroscopy by the resonance at 3.52 ppm [10–12,14,15] (Fig. 4). Indeed, the same complex was formed upon mixing equimolar amounts of *cis*-$[Pd(en)(H_2O)_2]^{2+}$ and the amino acid glycine.

5. Concluding remarks

The reaction between $PdCl_2$, or K_2PdCl_4, and diethanolamine in a molar ratio of 1:2, leads to the easy formation of the *trans*-$[PdCl_2(DEA)_2]$ complex, with the palladium(II)

ion being coordinated in an almost ideal square-planar fashion. in The reaction between the *trans*-$[PdCl_2(DEA)_2]$ or the *trans*-$[Pd(H_2O)_2(DEA)_2]^{2+}$ complex with MeCOHis-Gly dipeptide at $1.5 < pH < 2.0$ and at 25 °C results in the regioselective cleavage of the amide bond involving the carboxylic group of the histidine. No other dipeptide bonds were cleaved under these experimental conditions during the course of 72 h. The cleavage of the dipeptide was fast and the reaction went almost to completion within less than one hour. The reactions of these two palladium(II) complexes with MeCOHis-Gly are much faster in comparison with palladium(II) complexes of the type *cis*-$[Pd(L)(H_2O)_2]^{2+}$ (L is diamine, or any other chelating bidentate ligand) [10–17]. For example, the cleavage of the scissile peptide bond in the MeCOHis-Gly dipeptide by the *cis*-$[Pd(en)(H_2O)_2]^{2+}$ complex was completed only after 72 h at a temperature of 60 °C [10,11]. No difference in the rate of reactivity between the two examined palladium(II) complexes was observed. Complete detachment of the coordinated diethanolamine (DEA) ligand from palladium(II) occurred in the reaction with MeCOHis-Gly. The detachment of the coordinated amine ligand leads to the formation of the corresponding palladium(II) aqua complex. The formation of this complex as an intermediate catalytically active form can be the crucial step of the investigated reaction responsible for the fast hydrolysis of the dipeptide. This study indicates a direction for the development of new palladium(II) complexes and for their future application in biochemistry and structural biology.

6. Supplementary data

The crystallographic data is deposited with the Cambridge Crystallographic Data Centre. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +(44) 1223 336033; Telephone: +(44) 01223 762910; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk), quoting the deposition number CCDC 299671.

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