Metal Complexes of Biologically Important Ligands, CXII[+]

Bis(dipeptide ester–H^+) Complexes of Palladium(II) – Precursors for the Formation of Cyclotetrapeptides

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Dedicated to Professor Peter Jutzi on the occasion of his 60th birthday

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trans-Bis(dipeptide ester)palladium **1**–**6** complexes with a deprotonated amide group were obtained by dehydrochlorination of *trans*-Cl_2Pd(dipeptide ester)$_2$ or by direct reaction of Na_2PdCl_4 with dipeptide ester in the presence of sodium methoxide. The structure of $Pd(NH_2CH_2CONCH_2CH_2CO_2CH_3)_2$ (**3**) was determined by X-ray diffraction. Addition of $NaOCH_3$ to $Pd[NH_2C(H)(R)NCH_2CH_2CO_2CH_3]_2$ [R = $CH(CH_3)_2$ **4**, CH_2Ph **5**] results in the formation of the corresponding complexes **7**, **8** with cyclic tetrapeptides which also can be directly synthesized from the dipeptide ester and Na_2PdCl_4.

Introduction

Palladium(II) and platinum(II) complexes of amino acids and peptides have found considerable attraction due to their potential antitumor activity. Amino acid and peptide ligands may act as carriers for cyctotoxic metal fragments.[2] The chemistry of palladium(II)[3−5] and platinum(II)[3,6] with α-amino acids and peptides has been reviewed. Palladium(II) has many attractive features as a Lewis acid due to its fixed coordination number 4, its high Lewis acidity, its high formation constants with N,O donor ligands and its intermediate kinetic lability.[7] A particular feature of palladium(II) is its ability to deprotonate peptide NH groups, which in free peptides have pK_a values of ca. 15. The pK_a value of the Pd^{II}-induced ionization of peptide NH bonds is about 3.5[8], which is much lower than that of other metal ions such as Cu^{2+}, Ni^{2+} and Zn^{2+}.[9−11] Thus, Pd^{2+} ions show a nonspecific binding to the peptide backbone involving a destabilization of the secondary structure of peptides, i.e. α-helices.[12] The palladium ion promoted hydrolysis of peptides[13−15] and esters[7,15] has attracted attention due to the relevance of these systems to the function of metalloenzymes.[16] Ternary palladium complexes with peptides and nucleic acids were synthesized as models for the interaction between proteins and nucleic acids with the intervention of metal ions.[5,17,18] Several palladium complexes of peptides have been structurally characterized.[19−21]

Mogilevkina et al.[22] reported the synthesis of platinum(II) complexes $Pt(NH_2CH_2CONCH_2COOH)_2$ and $[Pt(NH_2CH_2CONCH_2CO_2)_2]^{2-}$ from Cl_2Pt(gly−glyOH)$_2$[23]. Margerum et al. studied the formation of (tripeptide)platinum complexes in solution.[24] From IR data a structure with N,N′ chelate rings was derived, like that found for the structurally characterized (Cl)Pt(gly−L-met).[25]

Results and Discussion

Recently we reported the metal-assisted formation of cyclic tetrapeptides from dipeptide esters.[26] In the course of our continuing studies on the formation of peptides at metal centres,[27−29] including the use of platinum(II) and palladium(II) as amino protecting group [6,30,31] we describe the synthesis and characterization of bis(dipeptide ester) complexes of palladium(II), which are precursors for the formation of cyclic peptides. The *trans*-bis(dipeptide ester) complexes of palladium(II) were obtained by two routes: a) by dehydrochlorination of *trans*-dichlorobis(dipeptide ester)palladium(II) with NEt_3 in dichloromethane to give **1** and **2** and b) by direct reaction of the dipeptide ester hydrochloride, consisting of α- and β-amino acids, with Na_2PdCl_4 in the presence of two equivalents of NaOMe in methanol to give **3**−**6**.

In the IR spectra the intensive absorptions at 1559−1580cm^{-1} and at 1722−1731 cm^{-1} are characteristic for the deprotonated and coordinated amide group and the ester group. The ^{1}H- and ^{13}C-NMR spectra show the expected signals. In accordance with *trans* configuration (C_2 symmetry) of **1**−**6** the peptide ligands show only one set of signals in the ^{1}H- and ^{13}C-NMR spectra. All compounds contain two supramolecularly bound equivalents of water

[+] Part CXI: see ref.[1]

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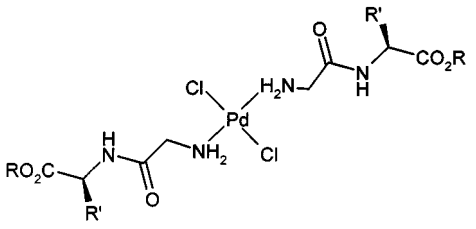
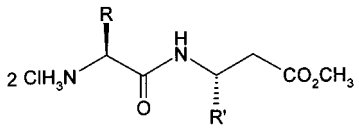
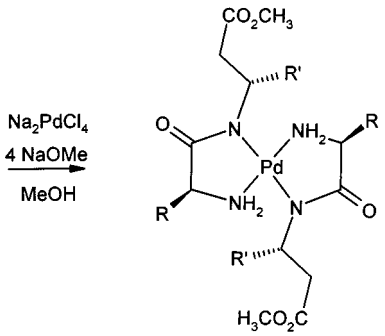


	R	R′
1	*t*Bu	H
2	Et	CH_2Ph

Scheme 1. Synthesis of *trans*-bis(dipeptide ester)Pd^{II} complexes by dehydrochlorination of *trans*-dichlorobis(dipeptide ester)Pd^{II} complexes





	R	R′
3	H	H
4	$CH(CH_3)_2$	H
5	CH_2Ph	H
6	H	CO_2CH_3

Scheme 2. Synthesis of *trans*-bis(dipeptide ester)Pd^{II} complexes by direct reaction of the dipeptide ester hydrochloride and Na_2PdCl_4

which can be observed in the ^{1}H-NMR spectra by a broad signal at $\delta \approx 4.6$.

Crystals of **3** were obtained by slow cooling of a saturated solution in methanol. The environment of the palladium atom is strictly planar (sum of the angles around the Pd atom is 360°). The X-ray crystal structure analysis of **3** × 4 H_2O shows the expected *trans* configuration with

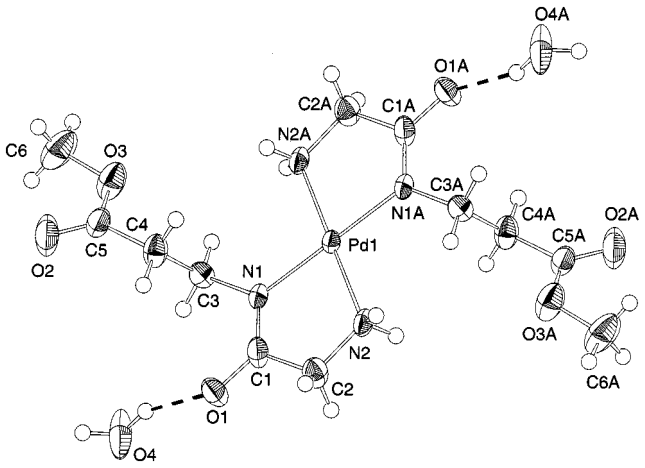


Figure 1. Molecular structure of **3** in the crystal; selected bond lengths [Å] and angles [°]: Pd−N(1) 2.010(6), Pd−N(2) 2.033(5), Pd−N(1A) 2.010(6), Pd−N(2A) 2.033(5), N(1)−C(1) 1.289(9), N(1)−C(3) 1.481(8), N(2)−C(2) 1.500(9), C(1)−C(2) 1.501(9), C(3)−C(4) 1.529(10), C(4)−C(5) 1.498(10), O(1)−C(1) 1.267(9), O(2)−C(5) 1.203(9), O(3)−C(5) 1.324(9), O(3)−C(6) 1.446(10); N(1A)−Pd−N(1) 180.0, N(1A)−Pd−N(2A) 81.5(2), N(1)−Pd−N(2A) 98.5(2), N(1A)−Pd−N(2) 98.5(2), N(1)−Pd−N(2) 81.5 (2), N(2A)−Pd−N(2) 180.0(1)

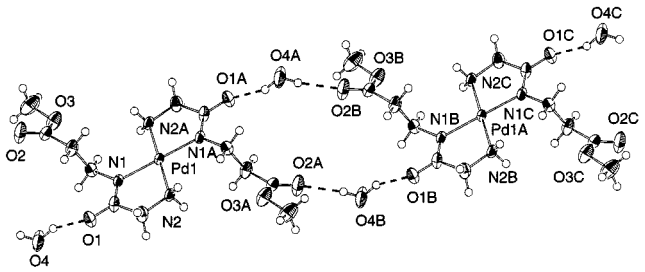


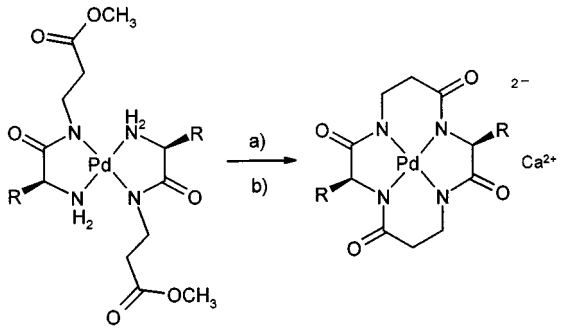
Figure 2. Part of the chain structure formed by the molecules of **3**

coordination of the amino and the deprotonated amide groups and with palladium as inversion centre (Figure 1). In the crystal lattice the molecules of **3** form chains via hydrogen bonds between the water molecules and the carbonyl groups of the amide and the ester groups (distance O1B···HO4B 1.856 Å, O2A···HO4B 2.023 Å, Figure 2). Similar hydrogen bonds between water molecules and carbonyl groups have been observed in the palladium complex [cyclo(gly−ß-ala)$_2$Pd](PPN)$_2$ × 8 H_2O × 3 CH_3CN which lead to the formation of layers.[26]

Addition of two equivalents of NaOMe to **4** and **5** results in the formation of the palladium complexes of cyclic tetrapeptides **7** and **8** which can also be directly obtained from a dipeptide ester and Na_2PdCl_4 (Scheme 3). Thus, the suggested mechanism[26] for the formation of cyclic tetrapeptides at some metal centres from dipeptide esters is proven.

The IR spectra of **7** and **8** show the characteristic intensive absorption for the amide group at 1560−1670 cm^{-1}. The ^{1}H-NMR spectra of **7** and **8** reveal broad signals according to a coordination of the calcium cation to the cyclic tetrapeptide.

A similar chelate complex of platinum(II) with two deprotonated tripeptide ligands **10** has been obtained by dehydrochlorination of *trans*-Cl_2Pt(gly−gly−glyOH)$_2$ (**9**) with

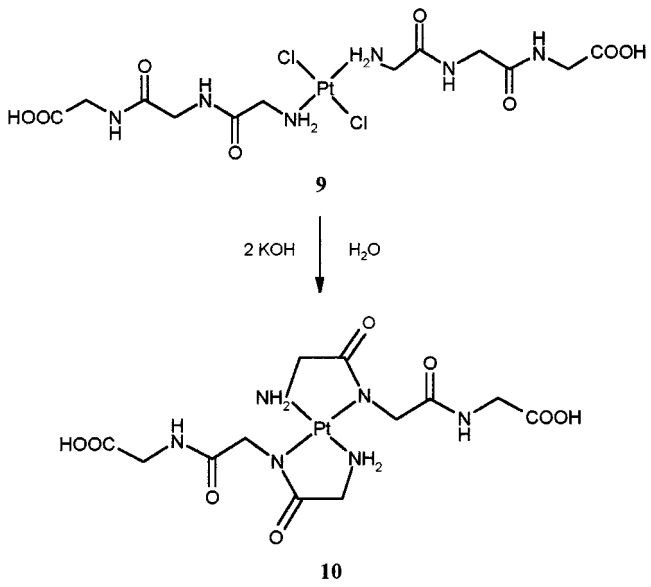


4, 5

	R
7	$CH(CH_3)_2$
8	CH_2Ph

Scheme 3. Formation of cyclotetrapeptide complexes: a) 2 NaOMe, MeOH, 24 h, 65°C; b) $CaCl_2$, acetone, H_2O

KOH. The latter was analogously synthesized as described for $Cl_2Pt(gly-alaOH)_2$.[32] Complex **10** can be further deprotonated with NaOH in aqueous solution to give $Na_2[Pt(NH_2CH_2CONCH_2CONHCH_2CO_2)_2]$ (**11**).



9

10

Scheme 4. Formation of complex **10**

Experimental Section

The *trans*-dichlorobis(dipeptide ester)Pd^{II} complexes were prepared as previously described.[33] Dipeptide ester hydrochlorides were prepared according to standard methods.[34,35] All operations were carried out under nitrogen using Schlenk techniques. Solvents were dried by distillation from Mg (MeOH), calcium hydride (CH_2Cl_2) or Na (Et_2O). − NMR spectra: Jeol EX 400 (^1H: 399.78 MHz; ^{13}C: 100.53 MHz). − IR: Perkin Elmer 841, Nicolet 520 FT-IR. − X-ray: NONIUS CAD4 diffractometer.

General Procedure for the Synthesis of 1 and 2: To a solution of *trans*-dichlorobis(dipeptide ester)palladium(II) (0.2 mmol) in 10 mL of dichloromethane NEt_3 (0.4 mmol) was slowly added. The solution was stirred for 3 d at room temperature, while the colour changed to light yellow. After concentration, the solid residue was washed twice with a small amount of water. The precipitate was centrifuged off and dried in vacuo.

1: Light yellow powder, yield 42%; m.p. 176°C (dec). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3280 s, 3230 s (NH_2), 1730 vs (ester), 1673 m, 1570 vs, br. (amide I). − $C_{16}H_{30}N_4O_6Pd$ (480.9): calcd. C 39.96, H 6.29, N 11.65; found C 39.70, H 6.39, N 10.41.

2: Light yellow powder, yield 25%; m.p. 110°C (dec). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3280 s, 3240 s (NH_2), 1720 vs (ester), 1670 m, 1570 vs, br. (amide I). − $C_{26}H_{34}N_4O_6Pd$ (605.0): calcd. C 51.61, H 5.66, N 9.26; found C 51.28, H 5.68, N 8.37.

General Procedure for the Synthesis of 3−6: In a typical experiment the dipeptide ester hydrochloride (0.2 mmol) and Na_2PdCl_4 (0.1 mmol) were dissolved in methanol (5 mL) and NaOMe (0.4 mmol) was slowly added to the solution. The light yellow reaction mixture was stirred for 1 h at room temperature. Then the solvent was evaporated in vacuo and the residue was dissolved in 10 mL of absolute dichloromethane. To achieve complete dissolution a minimum volume of absolute methanol was added. After centrifugation, the solution was concentrated to a volume of approximately 2 mL and the *trans*-bis(dipeptide ester)palladium(II) complexes were precipitated by addition of 40 mL of Et_2O as colourless powders, which were dried in vacuo.

3: Light yellow platelets, yield 76%; m.p. 165°C (dec.). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3332.5 vs, 3299.2 s (NH_2), 1731.3 vs (ester), 1564.1 vs, br. (amide I). − ^1H NMR (400 MHz, CD_3OD/D_2O): δ = 3.73 (s, 3 H, CO_2H_3), 3.35 (s, 2 H, CH_2), 3.04 (pseudo t, $^2J = {}^3J$ = 6.64 Hz, 2 H, NCH_2CH_2CO), 2.52 (pseudo t, $^2J = {}^3J$ = 6.64 Hz, 2 H, NCH_2CH_2CO). − ^{13}C NMR (100 MHz, CD_3OD/D_2O): δ = 183.00 (CONR), 176.86 (CO_2CH_3), 53.30 (CH_2), 42.46 (NCH_2CH_2CO), 35.65 (NCH_2CH_2CO). − $C_{12}H_{22}N_4O_6Pd \times H_2O$ (442.77): calcd. C 32.55, H 5.46, N 12.65; found C 33.35, H 5.47, N 12.04.

4: Colourless powder, yield 67%; m.p. 125°C (dec.). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3230 s, 3125 s (NH_2), 1728.8 vs (ester), 1559.4 vs, br. (amide I). − ^1H NMR (300 MHz, CD_3OD): δ = 3.63 (s, 6 H, CO_2CH_3), 3.47 [pseudo quint, ^2J = 5 Hz, ^3J = 7 Hz, 2 H, $CHCH(CH_3)_2$], 3.11−3.16 (m, 4 H, $NCH_2CH_2CO_2CH_3$), 2.53−2.46 [m, 2 H, $CHCH(CH_3)_2$], 2.36−2.30 (m, 4 H, $NCH_2CH_2CO_2CH_3$), 1.10 [d, ^3J = 7 Hz, 6 H, $CHCH(CH_3)_2$]. − ^{13}C NMR (300 MHz, CD_3OD): δ = 183.16 (CONR), 174.72 (CO_2CH_3), 66.09 [$CHCH(CH_3)_2$], 52.31 (CO_2CH_3), 41.93, 36.83 (CH_2CH_2), 32.59 [$CHCH(CH_3)_2$], 20.01, 18.09 [$CHCH(CH_3)_2$]. − $C_{18}H_{34}N_4O_6Pd \times 3\ H_2O$ (562.96): calcd. C 38.40, H 7.16, N 10.16; found C 37.99, H 6.40, N 9.95.

5: Colourless powder, yield 68%; m.p. 158°C (dec.). − IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3385.0 s, 3274.8 s, 3232.9 s (NH_2), 1721.7 vs (ester), 1568.9 vs, br. (amide I). − ^1H NMR (300 MHz, CD_3OD): δ = 7.36−7.17 (m, 10 H, Ph), 3.53 (dd, ^3J = 3.59 Hz, ^3J = 9.34 Hz, 2 H, $CHHCH$), 3.23 (dd, ^3J = 3.59 Hz, ^2J = 14.23 Hz, 2 H, $CHHCH$), 3.15 (pseudo t, $^3J = {}^2J$ = 7.48 Hz, 4 H, NCH_2CH_2CO), 3.03 (dd, ^3J = 9.34 Hz, ^2J = 14.23 Hz, 2 H, $CHHCH$), 2.46 (pseudo t, $^3J = {}^2J$ = 7.48 Hz, 4 H, NCH_2CH_2CO). − ^{13}C NMR (300 MHz, CD_3OD): δ = 182.38 (CONR), 174.52 (CO_2CH_3), 138.27, 130.68, 129.90, 128.14 (Ph), 62.02 ($CHCH_2$), 42.03, 41.08, 36.68 ($CHCH_2$ and CH_2CH_2). − $C_{26}H_{34}N_4O_6Pd \times 2.5\ H_2O$ (650.04): calcd. C 48.04, H 6.04, N 8.62; found C 47.91, H 5.68, N 8.70.

6: Colourless powder, yield 63%; m.p. 121°C (dec.). − IR (KBr, cm^{-1}) : $\tilde{\nu}$ = 3293.7 s, 3223.6 s (NH_2), 1721.8 vs (ester), 1580.4 vs,

br. (amide I). − ^{1}H NMR (300 MHz, CD_3OD): δ = 3.75, 3.70 (2 s and m, 14 H, 2 CO_2CH_3 and $CHCH_2$), 3.35 (d, 2 H, *H*CH), 3.2 (d, 2 H, HC*H*), 3.06 (dd, ^3J = 5.57 Hz, ^2J = 16.93 Hz, 2 H, CH*H*CH), 2.84 (dd, ^3J = 8.02 Hz, ^2J = 16.93 Hz, 2 H, CHHC*H*). − ^{13}C NMR (300 MHz, CD_3OD): δ = 183.42 (CONR), 175.45, 174.99 (2 CO_2CH_3), 57.50 ($CHCH_2$), 53.16, 53.08, 52.97 (CH_2, 2 CO_2CH_3), 37.06 ($CHCH_2$). − $C_{16}H_{26}N_4O_{10}Pd \times 2\ H_2O$ (576.86): calcd. C 33.31, H 5.24, N 9.71; found C 33.02, H 4.87, N 9.43.

X-ray Structure Determination of 3:[36] $C_{12}H_{22}O_6N_4Pd \times 2\ H_2O$, M = 460.77, T = 21(2)°C, NONIUS CAD4 diffractometer, crystal size, 0.17 × 0.27 × 0.50 mm, monoclin $P2_1/c$ (no. 14), a = 11.939(5), b = 7.814(3), c = 10.250(4), β = 96.38(2)°, V = 950.3(7) Å^3, Z = 2, d(calcd.) = 1.620 g/cm^3, λ(Mo-K_α) = 0.71073 Å, μ(Mo-K_α) = 1.021 mm^{-1}, F(000) = 472, 2θ range: 3.12−22.96°, index ranges: $-13 \le h \le 13$, $0 \le k \le 8$, $-11 \le l \le 0$, reflections collected: 1219, independent reflections: 1144 [R(int) = 0.0401], observed reflections: 941, semiempirical absorption correction from ψ scans, max./min. transmission: 0.9594/0.5076, data/restraints/parameters: 1144/0/116, refinement method: full-matrix least squares on F^2, goodness-of-fit on F^2: 1.077; final R indices [$I > 2\ \sigma(I)$]: $R1$ = 0.0491, $wR2$ = 0.1379; R indices (all data): $R1$ = 0.0579, $wR2$ = 0.1506, largest diff. peak/hole: 0.833/−0.787 eÅ^{-3}.

General Procedure for the Synthesis of 7 and 8: The *trans*-bis(dipeptide ester)Pd^{II} complex **4** or **5** (0.1 mmol) is dissolved in 10 mL of methanol. A solution of NaOMe (0.2 mmol) in methanol is added and the solution is heated to 65°C for 24 h, after which $CaCl_2$ (0.1 mmol) is added. Upon the addition of acetone the white precipitate is collected and for purification recrystallized from water/acetone (1/5), twice washed with acetone and dried in vacuo.

7: White powder, yield 89%. − IR (KBr, cm^{-1}): ṽ = 1560 vs, br. (amide I), 1417 s (amide II). − ^{1}H NMR (400 MHz, D_2O/CD_3OD): δ = 3.62−3.75 [m, br., 2 H, C*H*CH$(CH_3)_2$], 3.53−3.59 (m, br., 2 H, N*H*CHHCHCO), 3.5−2.92 (m, br., 4 H, NHC*HH*CHCO), 2.86−2.69 [m, br., 2 H, CHC*H*$(CH_3)_2$], 2.55−2.22 (m, br., 2 H, NHCHHC*H*CO), 1.10−1.14 [m, br., 12 H, CHCH$(CH_3)_2$]. − $C_{24}H_{24}CaN_4O_4Pd \times 8\ H_2O$ (683.025): calcd. C 39.86, H 5.58, N 7.75; found C 39.19 H 4.66, N 7.45.

8: White powder, yield 92%. − IR (KBr, cm^{-1}): ṽ = 1569 vs, br. (amide I), 1448 s, 1428 s, 1413 s (amide II). − ^{1}H NMR (400 MHz, D_2O/CD_3OD): δ = 6.98−7.45 (m, 10 H, C_6H_5), 4.20−4.45 (m, br., 2 H, C*H*CH_2Ph), 3.18−2.63 (m, br., 6 H, N*H*CHCH$_2$CO, CHC*H*$_2$Ph), 2.44−1.87 (m, br., 6 H, NHC*HCH*$_2$CO). − $C_{16}H_{24}CaN_4O_4Pd \times 3\ H_2O$ (536.938): calcd. C 35.79, H 5.63, N 10.43; found C 35.83 H 5.59, N 9.98.

9: The synthesis of **9** was accomplished according to Mogilevkina et al.[32] K_2PtCl_4 (420 mg, 1 mmol) and gly−gly−glyOH (760 mg, 4 mmol) were dissolved in 10 mL of 0.25 N NaOH (4 mmol) and the mixture was stirred for 40 min at 60°C in a water bath, while the colour of the solution changed from red to light yellow. After ice cooling the solution was combined with 2.5 mL of concentrated HCl and stirred for another 3 d at room temperature. The light yellow precipitate was collected and washed with HCl (2 N), ethanol and diethyl ether and dried in vacuo. − Light yellow powder, yield 34%; m.p. 196°C (dec.). − IR (KBr, cm^{-1}): ṽ = 3330 s, 3270 sh, 3230 sh (NH_2), 1720 m (COOH), 1650 vs (amide I), 1535 s (amide II). − $C_{12}H_{22}Cl_2N_6O_8Pt$ (644.3): calcd. C 22.27, H 3.44, N 13.04; found C 21.91, H 3.90, N 12.96.

10: A solution of 215 mg (0.33 mmol) of **9** in 1.33 mL of 0.5 N KOH (0.66 mmol) was stirred for 3.5 h at 70°C using a water bath. After stirring for 24 h at room temperature, the white precipitate was collected, washed with water, ethanol and diethyl ether and dried in vacuo. − Colourless powder, yield 21%; m.p. 206°C (dec.). − IR (KBr, cm^{-1}): ṽ = 3340 s, 3260 s (NH_2), 1700 vs (COOH), 1633 m, 1575 vs (amide I). − $C_{12}H_{20}N_6O_8Pt \times 2\ H_2O$ (607.5): calcd. C 23.73, H 3.98 N, 13.84; found C 23.82, H 3.69, N 13.61.

11: 170 mg (0.26 mmol) of **10** in 10.4 mL of 0.1 N NaOH (1.04 mol) was heated at 60°C for 8 h. After cooling to room temperature, the solution was added to acetone dropwise, whereby the white product precipitated, was collected and washed with acetone and dried in vacuo. − Yield 50%; m.p. 283°C (dec.). − IR (KBr): ṽ = 3280, 3230 sh (NH), 1633 s, 1575 w (amide), 1605 sh (CO_2^-). − $C_{12}H_{30}Na_2N_6O_{14}Pt \times 6\ H_2O$ (723.5): calcd. C 19.90, H 4.18, N 11.60; found C 19.87, H 3.71, N 11.49.

Acknowledgments

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