Metal Complexes of Biologically Important Ligands, CLXX [1]. Attachment of Unprotected Aminomonosaccharides and of 1,2-Diaminocyclohexane to Palladium(II) and Platinum(II) through Amino Acid and Peptide Residues

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Dedicated to Professor Wolfgang Steglich on the occasion of his 75th birthday

The reactions of unprotected D-glucosamine with *N*-coordinated, activated amino acid ester ligands (glycine, diglycine, histidine) of platinum(II) and palladium(II) complexes afford *cis*- and *trans*-$Cl_2Pt(NH_2CH_2CONHR)$, *trans*-$Cl_2Pt(NH_2CH_2CONHCH_2CONHR)_2$ and $Cl_2Pd(histNHR)_2$ (R = sugar residue) as products. 1,2-Diaminocyclohexane reacts with the activated esters of *cis*-$Cl_2Pt(NH_2CH_2COOH)_2$, *cis*-$Cl_2Pt(triglyOH)_2$, *cis*-$Cl_2Pt(metOH)$ and *cis*-$Cl_2Pd(histOH)$ to give dinuclear complexes $Cl_2Pt[(gly)_nNHC_6H_{10}NH(gly)_n]_2PtCl_2$ (n = 1, 3), $Cl_2Pt(methNHC_6H_{10}NHmeth)PtCl_2$ and $Cl_2Pd(histNHC_6H_{10}NHhist)PdCl_2$.

Key words: Glucosamine, 1,2-Diaminocyclohexane, Amino Acid, Platinum, Palladium

Introduction

Several platinum(II) and palladium(II) complexes with amino and diamino sugars or derivatives thereof have been synthesized and tested for antitumor activity [2 – 15], *e. g.* with the idea that the bioligands may function as carriers for the transport of the cytotoxic PtX_2 group [16] into tumor cells. Steinborn and Junicke have given a comprehensive review on carbohydrate complexes of platinum group metals [17]. In our group [2, 3, 18 – 22] a series of platinum complexes with protected and functionalized aminomonosaccharide ligands has been studied. We also could demonstrate that platinum(II) [and palladium(II)] are effective amino protecting groups for reactions at metal-coordinated α-amino acids and amino acid derivatives [2, 23 – 26].

Especially the Grinberg [27] and Volshtein complexes [28, 29], *trans*- and *cis*-$Cl_2Pt(NH_2CHRCO_2H)_2$, have been proven to be excellent starting compounds for these reactions. Thus, protected amino sugars [2] and amino-functionalized steroidal hormones could be attached to platinum(II) and palladium(II) through α-amino acid ligands as amides [26].

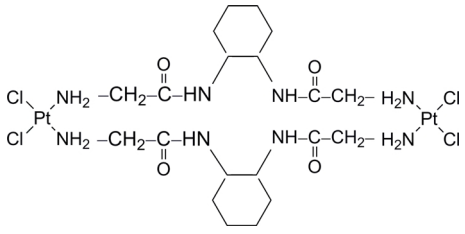
1,2-Diaminocyclohexane (dach) platinum complexes $(dach)PtX_2$ are a series of the most thoroughly studied antitumor compounds [16, 30, 31], and (1*R*,2*R*-dach)$Pt(C_2O_4)$ (Oxaliplatin) is an established drug in medicine [16].

In continuation of our studies on platinum complexes with sugar ligands we report on the binding of unprotected amino monosaccharides and of *R*,*R*-1,2-diaminocyclohexane through α-amino acids and peptides to palladium(II) and platinum(II).

Results and Discussion

For the preparation of complexes **1** – **8** a similar technique was applied as for the binding of amino-functionalized hormones or of amino acids to platinum or palladium [24, 26].

The activated esters of *cis*-$Cl_2Pt(NH_2CH_2COOH)_2$ [26, 28, 29], and *cis*-$Cl_2Pt(glyglyglyOH)_2$ (see Experimental Section), of $Cl_2Pt(methionine)$ [32] and of $Cl_2Pd(histidine)$ [33] were obtained by reaction with the water soluble *N*-ethyl-*N*′-[3-(dimethylamino)propyl] carbodiimide (EDC) as coupling agent and with *N*-hydroxy succinimide. The reactions of *R,R*,1,2-diaminocyclohexane with the activated esters afforded complexes **1** – **4**.



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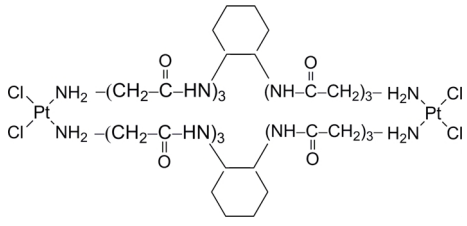

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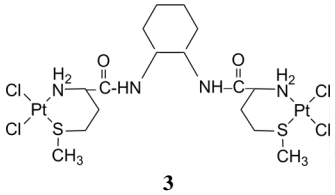

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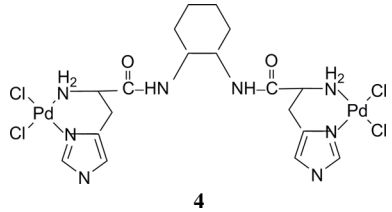

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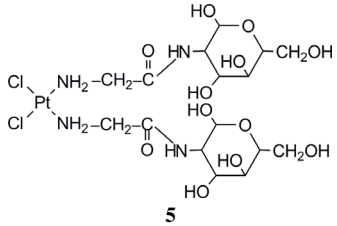

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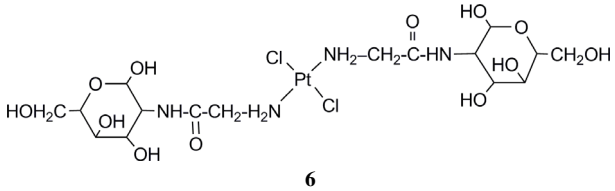

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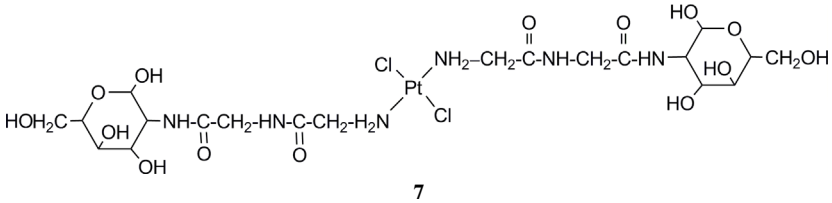

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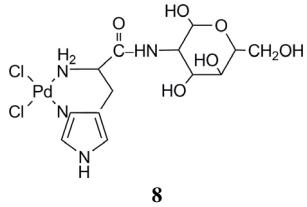

8

In complexes **1** and **2** the activated ester and diaminocyclohexane were used in the molar ratio 1 : 1; for the preparation of **3** and **4** a molar ratio of 2 : 1 was applied.

For complexes **1** – **4** a bimolecular structure has to be assumed. Polynuclear platinum complexes with bridging linkers have high potential for antitumor activity and may circumvent platinum resistance. These complexes have been studied most successfully and extensively by Farrell and coworkers [34] and also by other groups [16, 35]. Our group has studied bis(*cis*-dichloroplatinum) complexes with various bridged 1,2,4-triaminobutane units [36], with bis(imidazol-yl)alkanes [37] and polymethylene-bridged bis(ethylenediamine) compounds [38].

The IR spectra (Table 1) of complexes **1** – **4** exhibit characteristic absorptions at 3300 cm^{-1} (NH), 1660 cm^{-1} (amide I), 1540 cm^{-1} (amide II), and 320 cm^{-1} (Pt–Cl).

In the ^{1}H NMR spectra of **1** and **3** the signal of the amide group was observed at 8 ppm. The protons of the platinum-coordinated amino groups appear as a broad signal at 5.5 ppm. In the ^{1}H NMR spectrum of an aqueous (D_2O) solution of **2**, signals of NH protons are absent. Two broad resonances of the cyclohexane group were found at 1.7 and 1.2 ppm.

Complexes **5** – **8** were obtained – similarly as **1** – **4** – by reaction of the activated esters of *cis*-Cl_2Pt-($NH_2CH_2COOH)_2$ [26, 28, 29] and *trans*-Cl_2Pt(NH_2-$CH_2COOH)_2$ [27], *trans*-Cl_2Pt(glyglyOH)$_2$ [40] and Cl_2Pd(histidine) [33] with D-(+)-glucosamine.

During the reactions no deposition of elemental platinum was observed. However, the complexes decomposed slowly in aqueous solution. Characteristic IR absorptions of **4** – **8** are listed in Table 1. The absorptions of the solid complexes are broad which is due to hydrogen bonding. Complexes **2** and **5**, which are readily soluble in water, may be candidates for antitumor testing.

Table 1. Characteristic IR absorptions of **1** – **8** (in KBr).

		ν(NH)	CH aliph.		amide I	amide II	ν(M–Cl)
1		3220br,s	2930s		1655s,br	1548s,br	325m,br
		3100sh	2855m				
2		3320vbr,s	2928m		1655s	1533m	315w,br
		3080sh	2845w				
3		3320m	2923s		1665s	1540s	325sh
		3200s	2855w				310w
		3110m					
4		3200s	2920m		1653s	1540s	325w,br
		3110sh	2850w				
	ν(OH)	ν(NH)	CH aliph	ν(C=O)	amide I	amide II	ν(M–Cl)
5	3425s	3250sh	2930m	1735w	1660s	1550s	315w,br
		3130sh					
6	3360vbr	3280sh	2930m		1650s	1555s	330w
7	3350s	3100sh	2920m		1653s	1540s	325vw
	vbr						
8	3400s	3250s	2920m	1735m	1660s	1540s	320w,br
		3130sh					
9	3400s	3230s	2920w		1630s	1550s	320m
		3130sh					

Experimental Section

The starting complexes *cis*-$Cl_2Pt(NH_2CH_2COOH)_2$ [26, 28, 29], *trans*-$Cl_2Pt(glyOH)_2$ [27], *trans*-$Cl_2Pt(glyglyOH)_2$ [39], Cl_2Pt(methionine) [32], and Cl_2Pd(histidine) [33] were prepared as described in the literature.

cis-Dichloro-bis(glycylglycylglycine)-platinum(II), cis-$Cl_2Pt(glyglyglyOH)_2$

The synthesis of this complex was performed by following the procedure described by Mogilevkina [40] for the synthesis of *cis*- and *trans*-$Cl_2Pt(gly\text{-}alaOH)_2$.

0.83 g (2 mmol) of K_2PtCl_4 and 4 mmol of glycylglycylglycine were stirred in aqueous KOH solution (4 mmol KOH) for 3 d at r. t. The color of the solution changed from red to orange. The solution was evaporated *in vacuo* to dryness. The residue was dissolved in 4.5 mL of 1N hydrochloric acid, and the solution was again evaporated to dryness. The residue was dissolved in 4 mL of DMF and filtered. The orange solution was added dropwise to a 1 : 1 mixture of acetone/diethyl ether, and a pale orange solid was obtained. The product was purified by repeated precipitation from DMF/acetone – diethyl ether. The solid was centrifuged off, washed several times with diethyl ether and dried over P_2O_5 *in vacuo*. – Brown-yellow product. Yield 77 %. – Dec. 190 °C. – $Cl_2Pt(glyglyglyOH)_2 \cdot 1.5\,H_2O$, $C_{12}H_{25}Cl_2N_6O_{9.5}Pt$ (671.3): calcd. C 21.47, H 3.75, N 12.52; found C 22.06, H 4.05, N 12.19.

*Complexes **1** – **4***

1 mmol of *cis*-$Cl_2Pt(NH_2CH_2COOH)_2$, 1 mmol of *trans*-$Cl_2Pt(glyglyglyOH)_2$, 1 mmol of Cl_2Pt(methionine), or 1 mmol of Cl_2Pd(histidine) was dissolved in 10 mL of DMF and cooled to −10 °C. 2 mmol (0.23 g) of *N*-hydroxysuccinimide and then 2.2 mol (0.41 g) of *N*-ethyl-*N′*-(3-dimethyl-aminopropyl)carbodiimide (EDC) were added in portions. The mixture was stirred for 1 h at −10 °C and for 12 h at r. t. The yellow solution of the activated ester was filtered, and the filtrate was added dropwise to a mixture of 1 mmol (114 mg, for **1** and **2**) or 0.5 mmol (57 mg, for **3** and **4**) of (*R*,*R*)1,2-diaminocyclohexane and 2 mmol of NEt_3 in 10 mL of DMF at 0 °C. The mixture was stirred for 4 h at 0 °C and for 12 h at r. t. The solvent was removed *in vacuo*, and the residue was triturated five times with water. The water-soluble complex **2** could be purified by precipitation from water/ethanol. The complexes were dried *in vacuo* at 40 °C.

1: Pale yellow. Yield 60 %. Dec. 258 °C. – ^{1}H NMR (Jeol FX 90, [D_6]DMSO): δ = 8.06 br (CONH), 5.65, 5.12 br (NH_2), 1.70, 1.24, d, br (C_6H_{10}). – $C_{10}H_{20}Cl_2N_4O_2Pt \cdot H_2O$ (512.3): calcd. C 23.44, H 4.33, N 10.94; found C 23.71, H 4.09, N 10.81.

2: Beige. Dec. 211 °C. – ^{1}H NMR (Jeol FX 90, D_2O): δ = 3,87 s, 3.73 s, 3.54 m (CH_2), 1.66, 1.17 d, br (C_6H_{10}). – $C_{36}H_{64}Cl_4N_{16}O_{12}Pt_2 \cdot 5\,H_2O$ (1535.1): calcd. C 28.17, H 4.86, N 14.60; found C 28.51, H 4.95, N 14.10.

3: Beige. Yield 19 %. Dec. 249 °C. – ^{1}H NMR (Jeol FX 90, [D_7]DMF): δ = 8.26 br (CONH), 5.38 br (NH_2), 1.88 br, 2.27 br (CH_2), 1.68, 1.29 d, br (C_6H_{10}). – $C_{16}H_{32}Cl_4N_4O_2S_2Pt_2$ (908.6): calcd. C 21.15, H 3.55, N 6.17, S 7.06; found C 20.90, H 4.01, N 6.02, S 7.29.

4: Pale yellow. Yield 26 %. Dec. 251 °C. – $C_{18}H_{28}Cl_4N_8O_2Pd_2$ (743.1): calcd. C 29.09, H 3.80, N 15.08; found C 29.47, H 4.21, N 15.15.

*Complexes **5** – **8***

The complexes with the activated amino acid ester ligands were prepared as described for **1** – **4**: 0.3 mmol of *cis*-Cl_2-

$Pt(glyOH)_2$, 0.3 mol of *trans*-$Cl_2Pt(glyOH)_2$, 0.3 mmol of *trans*-$Cl_2Pt(glyglyOH)_2$, or 0.6 mol of $Cl_2Pd(hist)$ was dissolved in 10 mL of DMF and cooled to −10 °C. 2 mmol (0.23 mg) of *N*-hydroxysuccinimide and then, in portions, 2.2 mmol (0.51 mg) of EDC were added. The mixture was stirred for 1 h at −10 °C and then for 12 h at r.t. The yellow solution was filtered, and the filtrate was added dropwise to a Schlenk tube containing a solution of 0.6 mmol (129.2 mg) of D-(+)-glucosamine-hydrochloride and 1.5 mol (210 μL) of NEt_3 in 3 mL of DMF at 0 °C. After stirring for 12 h the solvent was removed *in vacuo*. Complexes **5**, **6** and **7** are soluble in water and can be purified by dissolution in a very small amount of water and precipitation with ethanol. This procedure can be repeated several times. Complex **8** is insoluble in water and was washed several times with water. The complexes were dried *in vacuo* at 40 °C.

5: Pale yellow. Dec. 171 °C. Yield 48 %. – $C_{16}H_{32}Cl_2N_2O_{12}Pt$ (738.5): calcd. C 26.02, H 4.37, N 7.59; found C 25.56, H 4.55, N 7.83.

6: Pale yellow. Dec. 184 °C. Yield 57 %. – $C_{16}H_{32}Cl_2N_4O_{12}Pt \cdot 2\,H_2O$ (774.5): calcd. C 24.81, H 4.69, N 7.23; found C 24.69, H 4.55, N 7.31.

7: Pale yellow. Dec. 171 °C. Yield 66 %. – $C_{20}H_{38}Cl_2N_6O_{14}Pt$ (852.5): calcd. C 28.18, H 4.49, N 9.86; found C 28.83, H 4.75, N 9.53.

8: Pale yellow. Dec. 215 °C. Yield 52 %. – $C_{12}H_{20}Cl_2N_4O_6Pd$ (493.6): calcd. C 29.20, H 4.08, N 11.35; found C 28.92, H 4.19, N 1.91.

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