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Reaction of [Pt(Gly-Gly-*N*,*N*′,*O*)I]$^-$ with the *N*-acetylated dipeptide L-methionyl-L-histidine: Selective platination of the histidine side chain by intramolecular migration of the platinum(II) complex

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ABSTRACT

The reaction of the monofunctional [Pt(Gly-Gly-*N*,*N*′,*O*)I]$^-$ complex, in which Gly-Gly is the dipeptide glycyl-glycine coordinated through two nitrogen and oxygen atoms, with the *N*-acetylated dipeptide L-methionyl-L-histidine (MeCOMet-His) studied by ^{1}H NMR spectroscopy. All reactions were carried out in 50 mM phosphate buffer at pD 7.4 and at 25 °C. In the initial stage of the reaction, the platinum(II) complex forms the kinetically favored [Pt(Gly-Gly-*N*,*N*′,*O*)(MeCOMet-His-*S*)]$^-$ complex, with unidentate coordination of the MeCOMet-His dipeptide through the sulfur atom of the methionine residue. In the second stage of the reaction, complete intramolecular migration of the [Pt(Gly-Gly-*N*,*N*′,*O*)] unit from the sulfur to the N3 nitrogen atom of imidazole was observed and a new platinum(II)-peptide complex, [Pt(Gly-Gly-*N*,*N*′,*O*)(MeCOMet-His-*N3*)]$^-$ was formed. In comparison with previous results obtained for the reaction of [Pt(dien)Cl]$^+$ with different methionine- and histidine-containing peptides, this migration reaction was sufficiently fast and strongly selective to the N3 atom of the imidazole ring of the histidine side chain. This study is an important step in the development of new platinum(II) complexes for selective covalent modification of peptides and proteins.

1. Introduction

In recent years, there has been an increasing interest in the interactions between platinum complexes and sulfur-containing biomolecules [1]. These interactions are thought to be responsible for a variety of biological effects, such as the inactivation of Pt(II) antitumor complexes, the development of cellular resistance to platinum drugs and toxic side effects, such as nephrotoxicity [2]. The thioether-containing amino acid methionine plays an important role in the metabolism of platinum anticancer drugs.

On the other hand, the presence of histidine has been established in a large number of the active centers of enzymes [3] and the histidyl residue is probably the most important metal-binding site in biological systems [4,5]. The heterocyclic imidazole ring system in the histidine side chain provides an ambidentate ligand with two competitive N3 and N1 donor atoms. In most metal complexes with histidine-containing ligands, the imidazole ring of histidine is coordinated through the N3 nitrogen [6–8] but relatively few complexes in which histidine is coordinated only through the N1 atom have been well characterized [9]. In biological systems, there are numerous metalloproteins in which a metal ion is bound to a histidine imidazole nitrogen only through N1 [10] (*e.g.* hemoglobin) but there are also metalloproteins in which a metal at the active site is bound through N3 of histidine [11] (*e.g.* Zn in superoxide dismutase) or has a mixed donor site sphere [11] [*e.g.* Cu in superoxide dismutase: $(N3)_2$, $N1_{term}$, $N1_{bridge}$] or where identical metals display different environments [12] [*e.g.* Cu_1-$(N3)_2$ and $Cu_3(N1)_8$ in ascorbate oxidase].

Peptides containing both methionine and histidine amino acids in the side chains have been shown to be good model molecules for the study their interactions with different platinum(II) complexes. Recently, it was found that platinum(II) complexes in the reactions with different methionine- and histidine-containing peptides initially react with the methionine sulfur atom while in the later stages, an intramolecular migration of the platinum(II) complex from a kinetically favored methionine side chain to a thermodynamically preferred imidazole N1 atom was observed [13–15]. Later results were surprising and in disagreement with those previously reported that nitrogen atoms from the imidazole ring of the amino acid histidine can not displace *S*-bound L-Met on a Pt(II) complex [16]. The discovering that an *S*-bound thioether ligand can be selectively displaced by one of the nitrogen atoms of the imidazole ring in the histidine side chain opens the possibility of designing new platinum complexes for selective covalent modification of proteins. In this work, an attempt was made to gain

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further insight into sulfur–nitrogen migration from a ^{1}H NMR spectroscopic study of the reaction of [Pt(Gly-Gly-*N,N′,O*)I]$^-$ with *N*-acetylated L-methionyl-L-histidine.

2. Experimental

2.1. Reagents

Distilled water was demineralized and purified to a resistance greater than 10 MΩ cm^{-1}. The compounds D_2O, DNO_3, NaOD and $K_2[PtCl_4]$ were obtained from the Aldrich Chemical Co. The dipeptides, glycyl-glycine (Gly-Gly), *S*-methylglutathione and L-methionyl-L-histidine (Met-His), were obtained from the Sigma Chemical Co. All common chemicals were of reagent grade. The terminal amino group in Met-His was acetylated by standard methods [17].

2.2. Syntheses of the platinum(II) complex

The complex K[Pt(Gly-Gly-*N,N′,O*)I] was prepared by a modification of a literature method [18]. To $K_2[PtCl_4]$ (0.2076 g, 5.00×10^{-4} mol) dissolved in 5 cm^3 of water was added 0.3320 g (2.00×10^{-4} mol) of KI and the mixture was heated at 60 °C for 5 min. Subsequently, an aqueous solution (5 cm^3) of the peptide glycyl-glycine (0.0660 g, 0.5 mM) was added to the obtained reaction mixture and the heating (60 °C) with stirring was continued for 30 min. During this time, the pH of the reaction mixture was controlled every 5 min and adjusted to about 6.5 with 1 M $KHCO_3$ solution. The obtained solution was concentrated to 5 cm^3 under vacuum and then left at room temperature over night. The obtained yellow crystals were filtered off, washed with ethanol and air dried. Yield 0.098 g (40%). Calculated for K[Pt(Gly-Gly-*N,N′,O*)I] = $C_4H_6N_2O_3IKPt$ (FW = 491.18): C, 9.78; N, 5.70; H, 1.23%; found: C, 9.63; N, 5.81; H, 1.34%. ^{1}H NMR (D_2O, 200 MHz); δ = 3.99 (s, 2H, CH_2) and δ = 3.62 (s, 2H, CH_2). ^{13}C NMR (D_2O, 200 MHz); δ = 51.72 (CH_2); δ = 53.37 (CH_2); δ = 182.55 (C═O) and δ = 194.00 (COO).

2.3. pH measurements

All pH measurements were made at room temperature. The pH meter (Iskra MA 5704) was calibrated with Fischer certified buffer solutions of pH 4.00 and 7.00. The results were converted into pD by the standard formula: pD = pH + 0.41 [19]. However, in conceptual references to acidity and basicity, the common symbol pH is used.

Elemental microanalyses for carbon, hydrogen, and nitrogen were performed at the Faculty of Chemistry of the University of Belgrade.

Table 1
Kinetic data for the reactions of Pt(II) complexes with thioether-containing ligands at 25 °C, where k_2 is the second-order rate constant

Reactants [complex + ligand]	pD value	$10^3\ k_2$/ $M^{-1}\ s^{-1}$	Ref.
[Pt(dien)Cl]$^+$ + L-Methionine	4.31	14	[16]
[Pt(dien)Cl]$^+$ + *S*-Methylglutathione	5.41	33	[21]
[Pt(dien)Cl]$^+$ + MeCOMet-His*	4.40	44	[13]
[Pt(Gly-Met-*S,N,N′*)I] + L-Methionine	4.31	4.5	[13]
[Pt(Gly-Met-*S,N,N′*)I] + *S*-Methylglutathione	4.34	0.3	This work
[Pt(Gly-Met-*S,N,N′*)I] + MeCOMet-His	4.40	8	This work
[Pt(Gly-Gly-*N,N′,O*)I]$^-$ + *S*-methylglutathione	4.21	40	This work
[Pt(Gly-Gly-*N,N′,O*)I]$^-$ + MeCOMet-His	4.11	70	This work

* MeCOMet-His is *N*-acetylated L-methionyl-L-histidine.

2.4. ^{1}H NMR measurements

The rate constants presented in Table 1 were obtained from ^{1}H NMR data measured using a Varian Gemini 200 spectrometer. The reactions were carried out in NMR tubes at 25 °C in 50 mM phosphate buffer at pD 7.4 in D_2O as the solvent. The platinum(II) complex and the peptide were mixed in a 1:1 molar ratio with 20 mM initial concentrations of both reactants and a final volume of 0.6 cm^3 in the NMR tube. The internal reference was TSP (sodium trimethylsilylpropane-3-sulfonate). The values of the rate constants for these reactions were determined when the data from the early part of the reactions (up to 2 h) were fitted to a second-order process [20] by plotting $x/a_o(a_o-x)$ against t (a_o is the initial concentration of the thioether ligand and x is the concentration of the Pt(II) complex with a *S*-bound thioether ligand at time t.

3. Results and discussion

The reaction of the monofunctional [Pt(Gly-Gly-*N,N′,O*)I]$^-$ complex, in which Gly-Gly is the dipeptide glycyl-glycine coordinated through two nitrogen and oxygen atoms, with the *N*-acetylated dipeptide L-methionyl-L-histidine (MeCOMet-His) was studied by ^{1}H NMR spectroscopy. This reaction was performed with equimolar amounts of the reactants in 50 mM phosphate buffer at pD 7.4 and at 25 °C. In the dipeptide MeCOMet-His, the terminal amino group had been acetylated to protect its coordination with platinum(II). The formation of the products in this reaction was monitored by ^{1}H NMR spectroscopic measurements of the chemical shifts of protons H2 and H5 of the imidazole ring in the histidine residue and the chemical shifts of the methyl protons in the methionine side chain. In the reaction with dipeptide MeCOMet-His the platinum(II) complex was stable under the above mentioned experimental conditions and release of chelated Gly-Gly ligand from Pt(II) first time was observed after 34 days. Two new signals at 3.82 and 3.86 ppm due to methylene glycine protons of the free Gly-Gly ligand were observed in the ^{1}H NMR spectrum. Addition of the dipeptide Gly-Gly to the reaction mixture caused an increase of these two signals. When the reaction of [Pt(Gly-Gly-*N,N′,O*)I]$^-$ with MeCOMet-His was carried out at a lower pD value ($2.0 \leqslant pD \leqslant 4.0$) release of Gly-Gly from Pt(II) was very fast and the replacement of this ligand with MeCO-Met-His dipeptide almost finished within 1 h.

3.1. Selective intramolecular migration of platinum(II) complex

Recently, a selective intramolecular migration of a platinum(II) complex from the methionine sulfur to the imidazole N1 atom was observed in the reaction between [Pt(dien)Cl]$^+$, in which dien is diethylenetriamine, with the *N*-acetylated dipeptide L-methionyl-L-histidine (MeCOMet-His) [13]. It was found that in the initial stages of this reaction, the [Pt(dien)Cl]$^+$ complex forms the kinetically favored [Pt(dien)(MeCOMet-His-*S*)]$^+$ complex with unidentate coordination of MeCOMet-His through the sulfur atom of the methionine residue. In the second stage of the reaction, an intramolecular migration of a [Pt(dien)]$^{2+}$ unit from the sulfur to the nitrogen atom of imidazole was observed. By ^{1}H NMR measurements, it was shown that this migration reaction is very slow and strongly selective to the N1 atom of the imidazole ring of the histidine side chain. No migration reaction of the platinum(II) complex was observed in the reaction between [Pt(Gly-Met-*S,N,N′*)Cl] (Gly-Met is the dipeptide glycyl-L-methionine coordinated through the sulfur and two nitrogen atoms) and the dipeptide MeCOMet-His [13]. It was found that the [Pt(Gly-Met-*S,N,N′*)Cl] complex, with a more sterically hindered Gly-Met ligand, reacts slower with thioether-containing molecules than [Pt(dien)Cl]$^+$ and forms a more stable platinum–sulfur bond (Table 1) [13,16,21].

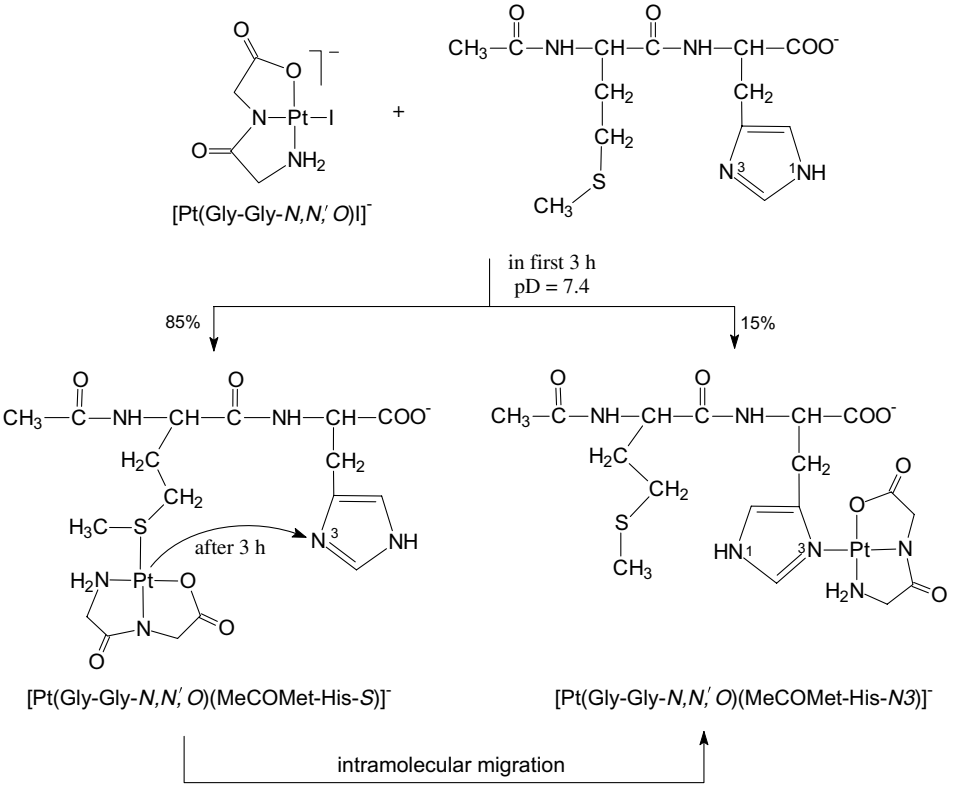
In the present study, the reaction of [Pt(Gly-Gly-*N,N′,O*)I]$^-$ with the *N*-acetylated dipeptide L-methionyl-L-histidine (MeCOMet-His) was performed at 25 °C in 50 mM phosphate buffer at pD 7.4. The corresponding Pt(II) complex and dipeptide were mixed in equimolar amounts and the formation of the products in these reactions was observed by ^{1}H NMR spectroscopic measurements. In the first 3 h, two platinum(II)-peptide complexes were observed in solution (see Scheme 1). The major product formed in a yield of 85% was the [Pt(Gly-Gly-*N,N′,O*)(MeCOMet-His-*S*)]$^-$ complex. In this complex, monodentate coordination of the peptide occurred through the sulfur atom of the methionine residue. The formation of [Pt(Gly-Gly-*N,N′,O*)(MeCOMet-His-*S*)]$^-$ is evident from the simultaneous decline of the resonances at 2.09 ppm, arising from the *S*-methyl protons of free MeCOMet-His, and the growth of the resonances at 2.55 and 2.57 ppm, corresponding to the *S*-methyl protons of the peptide coordinated to platinum(II) through the sulfur atom. The second product of the investigated reaction, formed in a yield of 15%, was [Pt(Gly-Gly-*N,N′,O*)(MeCOMet-His-*N3*)]$^-$. In the latter complex, monodentate coordination of the peptide occurred through the N3 nitrogen atom of the imidazole ring in histidine side chain. The characterization of this complex was performed by determining the chemical shifts of the protons H2 and H5 of the imidazole ring. In this complex, monodentate coordination of MeCOMet-His *via* the N3 atom of the imidazole ring shifts the H2 and H5 resonances to 7.11 and 8.05 ppm, respectively. These chemical shifts are consistent with those for the N3-isomer obtained in the reactions between different platinum(II) complexes with histidine and histidine-containing peptides (see Table 2) [13,22]. In the reaction of [Pt(Gly-Gly-*N,N′,O*)I]$^-$ with MeCOMet-His no coordination of platinum(II) complex to the N1 nitrogen atom of the imidazole ring in histidine side chain was observed. In accordance with our previous results for the reaction of [Pt(dien)Cl]$^+$ with MeCOMet-His monodentate coordination of platinum(II) complex to the N1 nitrogen atom of imidazole ring shifts the H2 and H5 resonances to 7.88 and 6.85 ppm, respectively (see Table 2) [13]. In the present study these resonances did not appear in the ^{1}H NMR spectra after 40 days.

Table 2
Proton chemical shifts of the H2 and H5 imidazole protons obtained in the reactions between different platinum(II) complexes with histidine and histidine-containing peptides

Peptide/complex	pD	Imidazole protons	
		H2	H5
MeCOMet-His	7.4	8.29	7.15
[Pt(dien)(MeCOMet-His-*N3*)]$^+$[a]	7.4	8.00	7.12
[Pt(dien)(MeCOMet-His-*N1*)]$^+$[a]	7.4	7.88	6.85
[Pt(Gly-Met-*S,N,N′*)(MeCOMet-His-*N3*)]$^+$[a]	6.8	8.04	7.16
[Pt(dien)(HisH$_2$-*N3*)]$^{2+}$[b]	6.8	8.04	7.25
[Pt(dien)(HisH$_2$-*N1*)]$^{2+}$[b]	6.8	7.92	6.94
[Pt(Gly-Gly-*N,N′,O*)(MeCOMet-His-*N3*)]$^-$[c]	7.4	8.05	7.11

[a] Ref. [13].
[b] Ref. [22].
[c] This work.

The reaction between [Pt(Gly-Gly-*N,N′,O*)I]$^-$ and MeCOMet-His was further followed after 3 h and the first change occurring in the ^{1}H NMR spectrum was the growth of the signal at 2.09 ppm, corresponding to the *S*-methyl protons of the free methionyl group of the MeCOMet-His peptide. The intensity of this signal was compared with those of the peaks at 2.55 and 2.57 ppm, arising from the *S*-methyl protons of the methionyl group bound to platinum(II). The latter two resonances slowly decreased in intensity. Simultaneously, the intensities of the resonances due to the H2 and H5 protons of the imidazole ring of the histidine side chain corresponding to platinum(II) bound to the N3 nitrogen atom slightly increased. These changes in the spectrum were caused by the breaking of the platinum(II)-sulfur bond and the release of the [Pt(Gly-Gly-*N,N′,O*)] unit from [Pt(Gly-Gly-*N,N′,O*)(MeCOMet-His-*S*)]$^-$, which had been initially formed in the reaction of [Pt(Gly-Gly-*N,N′,O*)I]$^-$ with the dipeptide MeCOMet-His. As a



Scheme 1.

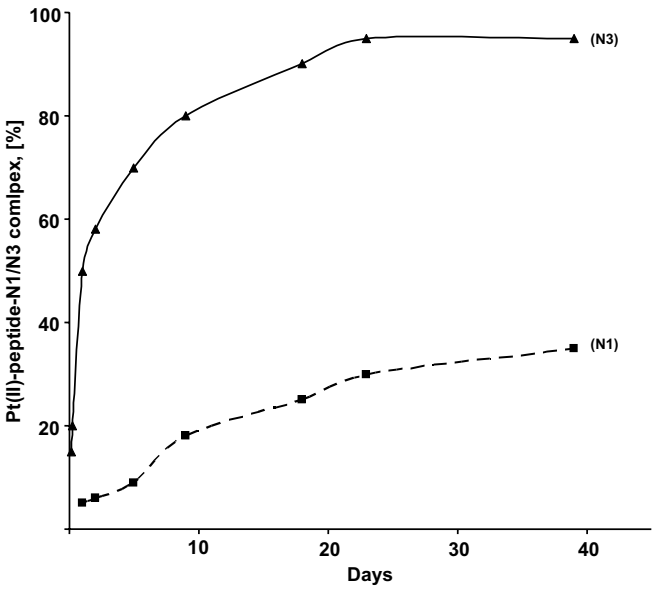


Fig. 1. Time dependence of Pt(II)–peptide–N1/N3 complex formation through the intramolecular migration of the Pt(II) complex from the methionine sulfur to the imidazole N1 ($[Pt(dien)Cl]^+$ (■)) or N3 ($[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ (▲)) nitrogen atom in the reactions between $[Pt(dien)Cl]^+$ and $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ with the MeCOMet-His dipeptide.

consequence of the cleavage of the platinum(II)–sulfur bond, the platinum(II)–peptide complex $[Pt(Gly\text{-}Gly\text{-}N,N',O)(MeCOMet\text{-}His\text{-}N3)]^-$ was formed (see Scheme 1). The total amount of $[Pt(Gly\text{-}Gly\text{-}N,N',O)(MeCOMet\text{-}His\text{-}N3)]^-$ formed in the latter stages of the reaction between $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ and MeCO-Met-His can be calculated from the integral values of the signals for the protons H2 and H5 for free imidazole and the corresponding values of these protons due to the N3 platinum(II) bound imidazole ring. The total concentration of $[Pt(Gly\text{-}Gly\text{-}N,N',O)(MeCOMet\text{-}His\text{-}N3)]^-$ formed after 10 days of reaction was *ca.* 80% (see Fig. 1). As can also be seen from Fig. 1, the intramolecular migration of the Pt(II) complex from the methionine sulfur to the imidazole N3 in the reaction of $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ with the dipeptide MeCO-Met-His was much faster in comparison with this process in the reaction of $[Pt(dien)Cl]^+$ with the MeCOMet-His dipeptide [13]. The intramolecular migration reaction displaced through the N3 imidazole nitrogen atom proceeds to almost complete platination of the MeCOMet-His dipeptide in the case of $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$, while in the case of the $[Pt(dien)Cl]^+$ complex, this platination reaction almost ceased with less than 40% coordinated to the N1 imidazole nitrogen atom (Fig. 1) [13].

3.2. Conclusions and prospects

The results from this study together with those obtained in previous studies [13–15] show that intramolecular migration of a platinum(II) complex from the *S*-bound thioether ligand to the nitrogen atom of the imidazole ring in histidine can occur under physiological pH conditions. In the reactions of $[Pt(dien)Cl]^+$ with MeCOMet-His and $[Pt(dien)(H_2O)]^{2+}$ with His-Met, His-Gly-Met and MeCOHis-Ala-Ala-Ala-MetNHPh peptides, intramolecular migration of the $[Pt(dien)]^{2+}$ unit from the methionine sulfur to the imidazole N1 atom was observed [13–15]. This migration process proceeded very slowly with incomplete platination of the histidine side chain in the investigated peptides. However, no migration of the platinum(II) complex was observed in the reaction between $[Pt(Gly\text{-}Met\text{-}S,N,N')Cl]$ and the dipeptide MeCOMet-His. This was explained through the fact that the latter complex reacts with the methionine sulfur atom five times slower than the $[Pt(dien)Cl]^+$ complex, forming thereby an extremely stabile platinum(II)-sulfur bond [13].

The present investigation shows that $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ in comparison with the $[Pt(dien)Cl]^+$ complex reacts approximately two times faster with the methionine sulfur atom from the dipeptide MeCOMet-His (see Table 1). This kinetically favored reaction forms thermodynamically labile platinum(II)-thioether bonds, which can be easily cleaved in the presence of a strong nucleophile at physiological pH values. In the reaction of $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ with MeCOMet-His, an intramolecular migration of the platinum(II) complex from the *S*-bound thioether ligand to the imidazole ring in the histidine side chain was observed. This migration reaction is strongly selective to the N3 nitrogen atom of imidazole. In comparison with $[Pt(dien)Cl]^+$ [13], the intramolecular migration reaction observed in the present study was much faster and proceeded to almost complete platination of the histidine side chain (see Fig. 1). The highest rate constant for $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ in comparison with those of other platinum(II) complexes observed for reactions with sulfur-containing donors (Table 1) and the very rapid intramolecular migration of this complex in the reaction with MeCOMet-His can be attributed to the *trans*-effect of the deprotonated peptide nitrogen and the large electronegativity value of the coordinated oxygen atom in the *cis*-position to the Pt—X bond (X is I^- or $-S\text{-}CH_3$). Both these factors contribute to the weakness of the Pt—X bond and together with the large size of the iodido ligand should obviously be taken in consideration when explaining the very fast reactivity of $[Pt(Gly\text{-}Gly\text{-}N,N',O)I]^-$ with the MeCOMet-His dipeptide. These latest results for the selective platination of the imidazole ring in dipeptides containing both methionine and histidine amino acids displaced through the intramolecular migration of a platinum(II) complex from the *S*-bound thioether ligand to the nitrogen atoms of imidazole can be employed in the design of new platinum(II) complexes for both the complete and selective covalent modification of proteins. Studies aimed at investigating these hypotheses are in progress.

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