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A comparative study of complex formation in the reactions of gold(III) with Gly-Gly, Gly-L-Ala and Gly-L-His dipeptides

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ABSTRACT

Proton NMR spectroscopy was applied to study the reactions of the dipeptides glycyl-glycine (Gly-Gly) and glycyl-L-alanine (Gly-L-Ala) with hydrogen tetrachloridoaurate(III) ($H[AuCl_4]$). All reactions were performed at pH 2.0 and 3.0 and at 40 °C. The final products in these reactions were [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl] complexes. Tridentate coordination of the corresponding dipeptides and square-planar geometry of these Au(III) complexes was confirmed by NMR (^1H and ^{13}C) spectroscopy. This study showed that at pH < 3.0 the Au(III) ion was able to deprotonate the amide nitrogen atom. However this displacement reaction was very slow and the total concentration of the corresponding Au(III)–peptide complex formed after 5 days was less than 60% for the Gly-L-Ala or 70% for the Gly-Gly dipeptide. The kinetic data of the reactions between the Gly-Gly and Gly-L-Ala dipeptides and $[AuCl_4]^-$ were compared with those for the histidine-containing Gly-L-His dipeptide. The differences in the reactivity of these three dipeptides with the Au(III) ion are discussed.

1. Introduction

Interest in Au(III) reactions with amino acids, peptides and proteins arises after it was proposed that Au(III) produced from Au(I) drugs might be involved in the toxic side-effects encountered in chrysotherapy [1–4]. In spite of these findings only a few investigations have been performed on the reactions of Au(III) with amino acids and peptides, and most of these investigations have focused on the sulfur-containing amino acids cysteine and methionine [5–13]. It was shown that Au(III) can oxidize the thiols to disulfides [5,6], can cleave the disulfide bond of cystine to give the sulfonic acid [5–8] and can oxidize the sulfur of methionine stereospecifically to the sulfoxide [9–13]. The structural consequences of these reactions can play an important role in the toxicity of Au(III), which precludes its use in chrysotherapy. The oxidation of protein disulfides by Au(III) will disrupt the secondary and tertiary structure of a protein, altering and probably preventing its normal biological function [7,8]. In fact, a recent survey of enzyme inhibition by Au complexes show Au(III) to be a much more potent inhibitor than Au(I) at equimolar concentrations [1]. However, from the current state of the art, it is surprising that investigations of the interactions of Au(III) with histidine-containing and other peptides are rather limited. Only three crystal structures of Au(III)–peptide complexes have been described previously: those of the dipeptides glycyl-L-histidine (Gly-L-His), [Au(Gly-L-His-$\kappa^3N_G,N_H,N3$)Cl]Cl·$3H_2O$ [14] and [Au(Gly-L-His-$\kappa^3N_G,N_H,N3$)]$_4$· $10H_2O$ [14] and glycyl-glycyl-L-histidine (Gly-Gly-L-His), [Au(Gly-Gly-L-His-$\kappa^4N_{G1},N_{G2},N_H,N3$)]Cl·$H_2O$ [15]. These complexes crystallized from a 1:1 reaction mixture at low pH (1.5–2.0) and their square-planar geometries were determined by X-ray analyses. From these investigations, it was found that the Au(III) ion has the capacity to deprotonate the histidine amide nitrogen in strong acidic solutions. NMR investigations of the reactions of the tripeptide glycyl-glycyl-glycine (Gly-Gly-Gly) with [Au(dien)Cl]Cl_2 complex showed that this complex at pH > 5.0 binds to the terminal amino nitrogen atom of this peptide [2]. No evidence was found for the involvement of the ether carboxyl or deprotonation of the amide nitrogen atom of the Gly-Gly-Gly tripeptide. The formation of the mononuclear Au(III)–peptide complexes, [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] and [Au(Gly-L-Ala-L-Ala-$\kappa^4N_G,N_{A1},N_{A2},O_{A2}$)]·$2H_2O$, was observed in the reactions of the L-alanine-containing peptides, glycyl-L-alanine (Gly-L-Ala) and glycyl-L-alanyl-L-alanine (Gly-L-Ala-L-Ala), with $H[AuCl_4]$ [16].

In view of the possible involvement of Au(III) in the immunological side-effects of Au therapy, further work on Au(III)–peptide interactions may help to improve the understanding of the immunochemistry of gold drugs. In light this statement, the present paper deals with a comparative study of the reactions between three dipeptides, glycyl-glycine (Gly-Gly), glycyl-L-alanine (Gly-L-Ala) and glycyl-L-histidine (Gly-L-His) with hydrogen tetrachloridoaurate(III) ($H[AuCl_4]$) at pH 2.0 and 3.0 and at 40 °C.

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2. Experimental

2.1. Reagents

Distilled water was demineralized and purified to a resistance greater than 10 M Ω cm^{-1}. The compounds D_2O, DCl, KOD and $H[AuCl_4]\cdot 3H_2O$ were obtained from the Aldrich Chemical Co. The dipeptides, glycyl-glycine (Gly-Gly), glycyl-L-alanine (Gly-L-Ala) and glycyl-L-histidine (Gly-L-His) were obtained from the Sigma Chemical Co. All common chemicals were of reagent grade.

2.2. Reactions of Gly-Gly and Gly-L-Ala dipeptides with $H[AuCl_4]$

The reactions of Gly-Gly and Gly-L-Ala dipeptides with $H[AuCl_4]$ were followed by ^{1}H NMR spectroscopy. Equimolar amounts of $H[AuCl_4]$ and dipeptide were mixed in an NMR tube with 40 mM initial concentration of both reactants. All reactions were performed at two different pH values, pH 2.0 and 3.0, and at 40 °C. Attempts to obtain crystallized Au(III)–dipeptide complexes for the reactions of Gly-Gly and Gly-L-Ala with $[AuCl_4]^-$ were unsuccessful and the [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl] complexes, as the final products in these reactions, were characterized by application of NMR (^{1}H and ^{13}C) spectroscopy.

2.3. Measurements

All pH measurements were made at room temperature. The pH meter (Iskra MA 5704) was calibrated with a Fischer certified buffer solution of pH 4.0. The results were not corrected for the deuterium isotope effect.

The ^{1}H and ^{13}C NMR spectra of D_2O solutions containing TSP (sodium trimethylsilylpropane-3-sulfonate) as the internal reference were recorded on a Varian Gemini 200 spectrometer.

2.4. Kinetics

All rate constants were obtained from ^{1}H NMR measurements. The reactions of Gly-Gly, Gly-L-Ala and Gly-L-His with $H[AuCl_4]$ were realized in NMR tubes at 25 °C in 1×10^{-3} M DCl in D_2O as solvent. The required dipeptide and $[AuCl_4]^-$ were mixed in a 1:1 M ratio with 40 mM initial concentrations of both reactants and a final volume of 0.6 cm^3. The reaction of Gly-L-His with $H[AuCl_4]$ was investigated previously and the final product of this reaction, the [Au(Gly-L-His-$\kappa^3N_G,N_H,N3$)Cl]Cl$\cdot 3H_2O$ complex, was characterized by X-ray crystallography [14]. In the present study, this reaction was investigated to compare its rate constant with those for the reactions of Gly-Gly and Gly-L-Ala with $[AuCl_4]^-$. The values of the rate constants for these reactions were determined when the data from the early part of the reactions (up to 3 h) were fitted to a second-order process [17] by plotting $x/a_0(a_0 - x)$ against t (where a_0 is the initial concentration of the free dipeptide and x is the concentration of the corresponding Au(III)–peptide complex containing tridentate coordinated Gly-Gly, Gly-L-Ala or Gly-L-His dipeptide at time t.

3. Results and discussion

3.1. NMR (^{1}H and ^{13}C) characterization of the Au(III)–dipeptide complexes

The reactions between two dipeptides, glycyl-glycine (Gly-Gly) and glycyl-L-alanine (Gly-L-Ala), and hydrogen tetrachloridoaurate(III) ($H[AuCl_4]$) were studied by ^{1}H NMR spectroscopy. All reactions performed at two different pH values (pH 2.0 and 3.0) and at 40 °C. The formations of the Au(III)–peptide complexes containing tridentate coordinated Gly-Gly and Gly-L-Ala dipeptides were observed; see Fig. 1. The characterization of the [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl] complexes, as the major products in these reactions, was realized by ^{1}H and ^{13}C NMR spectroscopy; see Tables 1 and 2. From the obtained spectroscopic data, it was concluded that coordination of these dipeptides to Au(III) ion occurred through the nitrogen atom of the terminal amino group, the deprotonated peptide nitrogen and the oxygen atom of the carboxyl group. The NMR data of the [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl] complexes indicate that the fourth coordination place in these square-planar complexes is a monodentate coordinated ligand, preferably chloride ion. From Tables 1 and 2, it can be seen that all ^{1}H and ^{13}C NMR resonances of [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-

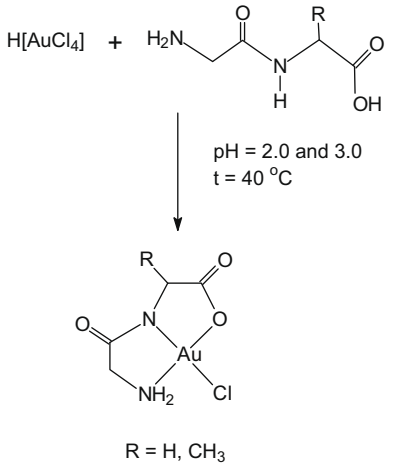

Fig. 1. Schematic representation for the reaction of Gly-Gly and Gly-L-Ala with $H[AuCl_4]$.

Table 1
Proton NMR chemical shifts (δ, ppm) for the Gly-Gly and Gly-L-Ala dipeptides and the corresponding Au(III)–peptide complexes, [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl], at pH 3.0 in D_2O as solvent with TSP as the internal standard[a].

Peptide/complex	Gly-Gly	[Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl]	Gly-L-Ala	[Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl]
Protons				
Gly1CH_2	3.89 (*s*)	3.96 (*s*)	3.84 (*s*)	3.90 (*s*)
Gly2CH_2	4.07 (*s*)	4.26 (*s*)		
AlaαCH			4.08 (*q*)	4.15 (*q*)
AlaβCH_3			1.40 (*d*)	1.44 (*d*)

[a] *s* = singlet; *d* = doublet; *q* = quartet.

Table 2
^{13}C NMR chemical shifts (δ, ppm) for the Gly-Gly and Gly-L-Ala dipeptides and the corresponding Au(III)–peptide complexes, [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl], at pH 3.0 in D_2O as solvent with TSP as the internal standard.

Peptide/complex	Gly-Gly	[Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl]	Gly-L-Ala	[Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl]
Carbon atoms				
Gly1CH_2	43.44	49.95	43.33	49.99
Gly2CH_2	45.79	50.25		
Gly1CO	170.00	176.06	169.06	175.99
Gly2COO	178.75	188.16		
AlaαCH			54.01	58.06
AlaβCH_3			20.00	22.34
AlaCOO			182.78	188.60

Ala-κ^3N_G,N_A,O_A)Cl] complexes with respect to those for the free Gly-Gly and Gly-L-Ala dipeptides were shifted downfield. These shifts between the NMR resonances of the Au(III) complexes and free dipeptides were caused by tridentate coordination of the dipeptides to Au(III) ion. Downfield shifting of the ^{1}H NMR resonances was observed previously for Gly-Gly-L-His upon its tetradentate coordination in the [Au(Gly-Gly-L-His-$\kappa^4N_{G1},N_{G2},N_H,N3$)]Cl·$H_2O$ complex [15]. Moreover, shifting of the ^{1}H NMR resonances between peptide and the corresponding Au(III) complex were also observed in the reaction of Gly-L-Ala with $[AuCl_4]^-$ at pH 4.0 [16]. The coordination of Gly-Gly and Gly-L-Ala dipeptides to Au(III) ion is a slow process and the rate of this reaction depends on pH (Fig. 2). When the reaction between these peptides and $H[AuCl_4]$ was performed at pH > 3.0 (pH 4.0 and 5.0), reduction of Au(III) occurred during time. This reduction process was much faster at higher pH values and the complete reaction mixture was dark from elemental Au(0) at pH 5.0 after 12 h at 40 °C.

3.2. Reaction of Gly-Gly with $[AuCl_4]^-$

The time dependence of the formation of the [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] complex in the reaction between Gly-Gly and $H[AuCl_4]$ at the pH 2.0 and 3.0 and at 40 °C was monitored by ^{1}H NMR spectroscopy; see Fig. 3a. The resonances at 3.89 ppm of the $Gly1CH_2$ and at 4.07 ppm of the $Gly2CH_2$ protons for the free peptide decreased and new resonances at 3.96 and 4.26 ppm, due to these protons for the tridentate coordinated peptide, increased with reaction time. The reaction was followed for 5 days and during this time the amount of [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] complex was calculated from the integral value of the signals for $Gly1CH_2$ and $Gly2CH_2$ protons of the free Gly-Gly and the corresponding values of these protons due to the tridentate coordinated peptide. The total amount of [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] complex formed after 5 days of reaction was 70%. The rate constant for this reaction was determined when the data from the early part of the reaction (up to 3 h) were fitted to a second-order process [17] by plotting $x/a_0(a_0 - x)$ vs. t (where a_0 is the initial concentration of Gly-Gly and x is the concentration of [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] at time t), yielding a rate constant of $(1.63 \pm 0.07) \times 10^{-7}$ M^{-1} s^{-1} (Table 3).

3.3. Reaction of Gly-L-Ala with $[AuCl_4]^-$

The reaction between Gly-L-Ala and $[AuCl_4]^-$ was performed under the same experimental conditions as those for Gly-Gly. The formation of the [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] complex is evident from the simultaneous decline of the singlet at 3.84 ppm and the doublet at 1.40 ppm, arising from the $GlyCH_2$ and AlaβCH_3 protons of the free Gly-L-Ala dipeptide, respectively, and the growth of the singlet at 3.90 ppm for $GlyCH_2$ and the doublet at 1.44 ppm for AlaβCH_3, corresponding to the tridentate coordinated Gly-L-Ala dipeptide; see Fig. 3b. The total amount of the [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] complex formed after 5 days of reaction was 55%. The concentration of the [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] complex with time was determined from the integral values of the signals at 3.84 and 3.90 ppm for $GlyCH_2$ protons of the free and coordinated Gly-L-Ala dipeptide, respectively (Fig. 3b). The second-order rate constant (k_2) for this reaction ($(0.71 \pm 0.06) \times 10^{-7}$ M^{-1} s^{-1}; see Table 3), was obtained by applying the method previously explained for the reaction of Gly-Gly with $[AuCl_4]^-$ [17].

3.4. Comparative study of the reactivity of Gly-Gly, Gly-L-Ala and Gly-L-His dipeptides with $[AuCl_4]^-$

In the reactions of Gly-Gly and Gly-L-Ala with $[AuCl_4]^-$ at pH 2.0 and 3.0 and at 40 °C, two Au(III)–peptide complexes, [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl] and [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl], were formed (Fig. 1). The NMR (^{1}H and ^{13}C) investigations (Tables 1 and 2) of these reactions showed that the Au(III) ion was capable of displacing the amide proton of the peptide bond under the above-mentioned experimental conditions. However, when the reactions of these two peptides with $[AuCl_4]^-$ were performed at pH > 3.0, the dominant process was the reduction of the Au(III) ion. The rate constant for the Au(III)–dipeptide complex formation in the reaction of Gly-Gly with $[AuCl_4]^-$ was found to be approximately two times higher than that for the reaction of the Gly-L-Ala dipeptide (Table 3). The difference in the reactivity between these two dipeptides can be attributed to the steric hindrance of the methyl group of L-alanine. The rate constants of Au(III)–peptide complex formation for the reactions between Gly-Gly and Gly-L-Ala dipeptides and $[AuCl_4]^-$ were compared with that for the reaction of the histidine-containing Gly-L-His dipeptide and $[AuCl_4]^-$; see Table 3. The Gly-L-His and $[AuCl_4]^-$ were reacted in a 1:1 M ratio at pH 3.0 and at room temperature and time dependence of the formation of the [Au(Gly-L-His-$\kappa^3N_G,N_H,N3$)Cl]$^+$ complex [14] was monitored from the integral values of the ^{1}H NMR resonances at 3.78 and 3.98 ppm due to the Gly protons of the free and coordinated Gly-L-His dipeptide, respectively. The second-order rate constant for this reaction ($(124.00 \pm 0.30) \times 10^{-7}$ M^{-1} s^{-1}; see Table 3) was

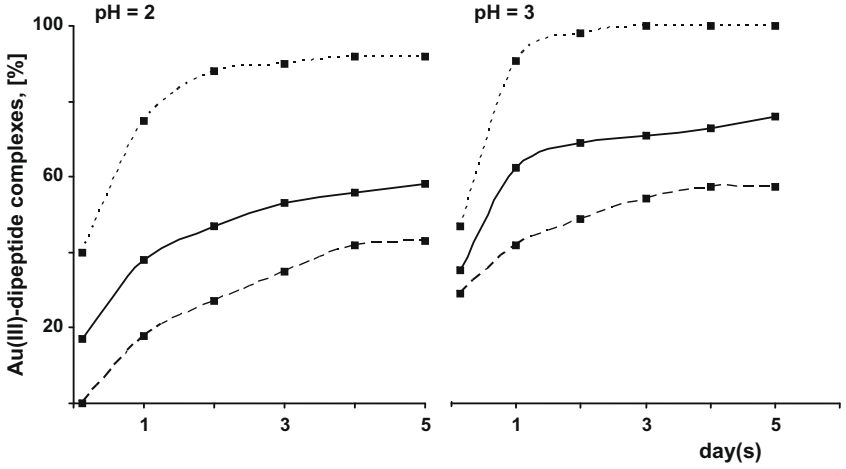

Fig. 2. Dependence of the formation of the [Au(Gly-Gly-$\kappa^3N_{G1},N_{G2},O_{G2}$)Cl], [Au(Gly-L-Ala-$\kappa^3N_G,N_A,O_A$)Cl] and [Au(Gly-L-His-$\kappa^3N_G,N_H,N3$)Cl]Cl complexes on the pH in the reactions of Gly-Gly (—), Gly-L-Ala (– – –) and Gly-L-His (···) with $H[AuCl_4]$ at 40 °C.

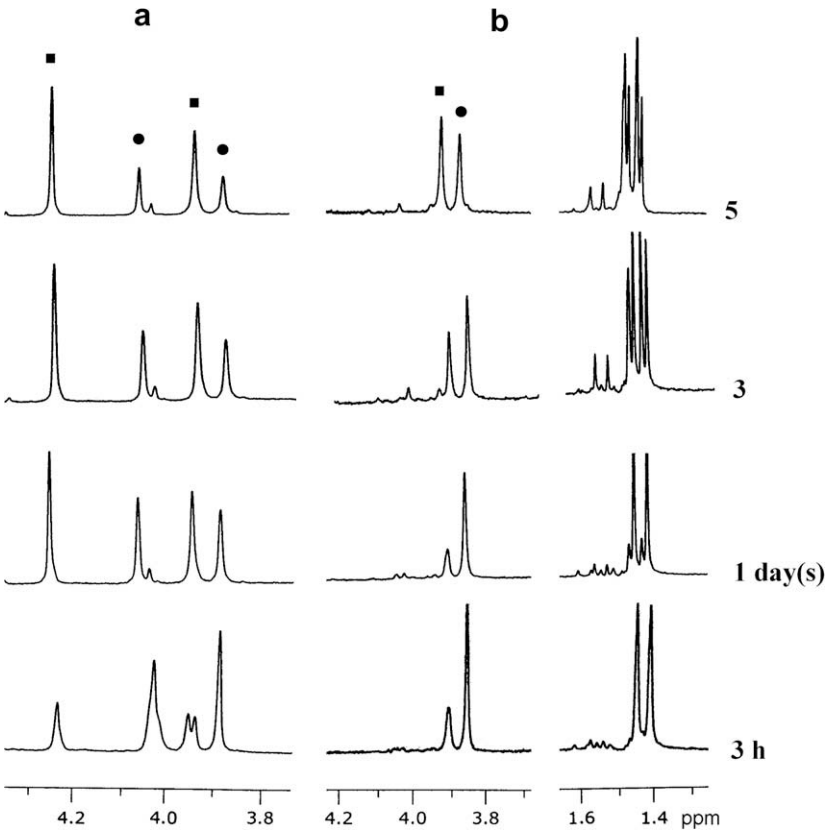

Fig. 3. Parts of the ^{1}H NMR spectra during the reaction of Gly-Gly (a) and Gly-L-Ala (b) with H[AuCl$_4$] as a function of time at pH 3.0 and at 40 °C in D_2O as solvent with TSP as the standard. Resonances are indicated as follows: (a) Gly-Gly + H[AuCl$_4$], (●) Gly1CH$_2$ at 3.89 and Gly2CH$_2$ at 4.07 ppm of the free dipeptide; (■) Gly1CH$_2$ at 3.96 and Gly2CH$_2$ protons at 4.26 ppm of the [Au(Gly-Gly-κ$^3N_{G1}$,N_{G2},O_{G2})Cl] complex; (b) Gly-L-Ala + H[AuCl$_4$], (●) GlyCH$_2$ at 3.84 ppm of the free dipeptide and (■) GlyCH$_2$ at 3.90 ppm of the [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] complex.

Table 3
Second-order rate constants (k_2) of the formation of Au(III)–peptide complexes for the reactions of Gly-Gly, Gly-L-Ala and Gly-L-His with [AuCl$_4$]$^-$ at 25 °C in 1×10^{-3} M DCl in D_2O as solvent.

Reactions	$k_2 \times 10^{-7}$ M^{-1} s^{-1}
Gly-L-Ala + H[AuCl$_4$] → [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl]	0.71 ± 0.06
Gly-Gly + H[AuCl$_4$] → [Au(Gly-Gly-κ$^3N_{G1}$,N_{G2},O_{G2})Cl]	1.63 ± 0.07
Gly-L-His + H[AuCl$_4$] → [Au(Gly-L-His-κ^3N_G,N_H,$N3$)Cl]Cl	124.00 ± 0.30

obtained by applying the same methods as those previously explained for the reaction of Gly-Gly or Gly-L-Ala with [AuCl$_4$]$^-$. From Table 3, it can be seen that these three dipeptides differed greatly in their reactivity with the Au(III) ion. The difference in the reactivity of these three dipeptides with the Au(III) ion is also clearly demonstrated in Fig. 2, which shows the time dependence of the formation of the Au(III)–peptide complex for the reactions of Gly-Gly, Gly-L-Ala and Gly-L-His with H[AuCl$_4$] at pH 2.0 and 3.0 and at 40 °C. From this figure, it is obvious that the concentrations of the Au(III)–peptide complexes formed during time were different. Difference in the yield for these three complexes, [Au(Gly-Gly-κ$^3N_{G1}$,N_{G2},O_{G2})Cl], [Au(Gly-L-Ala-κ^3N_G,N_A,O_A)Cl] and [Au(Gly-L-His-κ^3N_G,N_H,$N3$)Cl]$^+$, as well as difference in the reactivity of the corresponding dipeptides with Au(III) ion, can be attributed to the fact that the N3 nitrogen atom in the imidazole ring of the Gly-L-His dipeptide is a much stronger nucleophile than the other donor atoms present in the none histidine-containing dipeptides, Gly-Gly and Gly-L-Ala. The binding of Au(III) ion to the N3 nitrogen atom is the rate determining step in the formation of the [Au(Gly-L-His-κ^3N_G,N_H,$N3$)Cl]$^+$ complex. The N3-anchored Au(III) ion showed itself to be very effective in displacing of the amide proton and next step of this reaction was the very fast coordination of this metal ion to the deprotonated nitrogen atom of the amide bond and to the terminal amino group as the final step of the reaction, leading to the tridentate coordination of this peptide. Finally, from the present study it can be concluded that in acidic solution the histidine-containing Gly-L-His dipeptide is a better chelating ligand for Au(III) ion than the Gly-Gly and Gly-L-Ala dipeptides. This chelation reaction can contribute to the stabilization of the Au(III) oxidation state and to its protection from further reduction process, which easily occurs in the reactions of Au(III) with sulfur-containing peptides [5–13].

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