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Synthesis, spectroscopic, structural and theoretical characterization of hydrogensquarate and mononuclear Au(III)-complex of dipeptide phenylalanyltyrosine

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Abstract

The mononuclear Au(III)-complex ([$Au(C_{18}H_{18}N_2O_4)Cl$]) and hydrogensquarate ([$C_{22}H_{21}N_2O_8$]) of dipeptide phenylalanyltyrosine (*H–Phe–Tyr–OH*) have been synthesized, characterized spectroscopically and structurally by means of solid-state linear-polarized IR-spectroscopy, ^{1}H- and ^{13}C-NMR, ESI-MS, HPLC-MS–MS, FAB-MS, TGS and DSC methods. The structure of the Au(III)-complex has been predicted theoretically by DFT calculations. The dipeptide coordinated in a tridentate manner *via* $–NH_2$, $–COO^-$ and N^--groups. One Cl^- ion is attached to the metal centre as a terminal ligand, yielding a planar AuN_2OCl chromophor. The hydrogensquarate consists in positive charged dipeptide moiety and negative one hydrogensquarate (HSq^-) anion stabilizing by strong intermolecular hydrogen bonds.

Keywords: Solid-state linear-polarized IR-spectroscopy; ^{1}H- and ^{13}C-NMR; ESI-MS; HPLC-MS–MS; FABMS; TGS and DSC methods; H–Phe–Tyr–OH dipeptide; Au(III)-complexes; Hydrogensquarate

1. Introduction

Au(III)-complexes and salts of amino acid derivatives and peptides are of interest for a range of preparative and pharmaceutical applications as potential anticancer agents. Moreover, the investigations of complexation ability of these biological active compounds could be explained the way for coordination of metals to DNA in living cell [1–4]. Furthermore, the squaric acid salts with optically active amino acid amides crystallized noncentrosymmetrically and are of great interest for nonlinear optical and electro optical application [5–9]. In last years the bioactivity of squaric acid and some derivatives as inhibitors and VLA-4 integring antagonists [10] or potassium channel openers [11–13] have been also reported. These results have been in the basis of our previous spectroscopic and structural studies of some optically active hydrogensquarate derivatives of amino acids amides [8,9] as well as of Au(III)-complexes and salts with aliphatic and aromatic di- and tripeptides [14–19].

We now present a spectroscopic and theoretical characterization of hydrogensquarate and Au(III)-complex of dipeptide phenylalnyl–tyrosine (*H–Phe–Tyr–OH*) (Scheme 1) by means of linear-polarized IR-LD spectroscopy of oriented solid samples as a nematic liquid crystal suspension, ^{1}H- and ^{13}C-NMR, ESI-MS, HPLC-MS–MS, FAB-MS, TGS and DSC methods. The theoretical DFT calculations (B3LYP and Lanl2DZ (Au)/6-31+G(3df) (Cl, C, H)) using polarization function alpha 0.2 and 1.2 (Au) is also demonstrated, obtaining the structure of Au(III)-complex. As far

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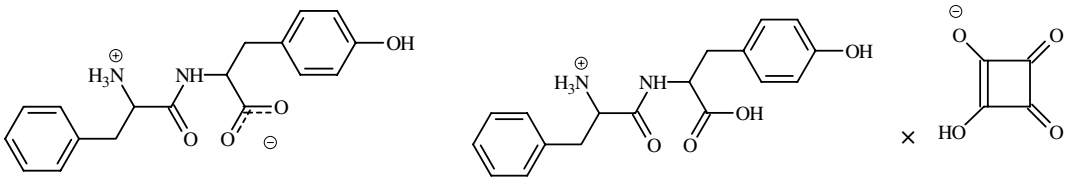


H-Phe-Tyr-OH *H_2Sq×H-Phe-Tyr-OH*

Scheme 1. Chemical diagram of compounds studied.

as the exact structures of the Au(III)-complexes with peptides are rare in the literature, only three structures with dipeptide glycylhistidine: ([(Au(H–Gly–L–His–OH)H_{-1})-Cl]Cl × $3H_2O$) and [(Au(H–Gly–L–His–OH)H_{-3})]$_4$ × $10H_2O$ and with tripeptide glycylglycylhistidine: [(Au(H–Gly–Gly–His–OH)H_{-2})]Cl × H_2O are known [20,21], and any studied, developing the new approaches for structural information receiving in solid state are reasonable.

2. Experimental

2.1. Materials and methods

The dipeptide *H–Phe–Tyr–OH* (⩾99.00%) was purchased from Bachem Organics (Switzerland) and was used without further purification.

The 4000–400 cm^{-1} solid-state IR-spectra were recorded on a Bomem Michelson 100 FT-IR spectrometer (resolution 2 cm^{-1}, 150 scans) equipped with a Perkin-Elmer wire-grid polarizer. The oriented solid samples were obtained as a suspension in a nematic liquid crystal of the 4′-cyano-4′-alkylbicyclohexyl type (ZLI 1695, Merck), mesomorphic at room temperature. Its weak IR-spectrum permits the recording of the guest-compound bands in the whole 4000–400 cm^{-1} range. The presence of an isolated nitrile stretching IR-band at 2236 cm^{-1} serves additionally as an orientation indicator. The effective orientation of the samples was achieved through the following procedure: 5 mg of the compound to be studied was mixed with the liquid crystal substance until a slightly viscous suspension was obtained. The phase thus prepared was pressed between two KBr-plates for which, in advance, one direction had been rubbed out by means of fine sandpaper. The grinding of the mull in the rubbing direction promotes an additional orientation of the sample [15–19].

IR-LD spectroscopy and the interpretation of the linear-polarized IR-spectra are described in [22–26]. The method consists of subtraction of the perpendicular spectrum, (IR_s, resulting from a 90° angle between the polarized light beam electric vector and the orientation of the sample) from the parallel one (IR_p) obtained with a co-linear mutual orientation. The recorded *difference* (IR_p–IR_s) spectrum divides the corresponding parallel (A_p) and perpendicular (A_s) integrated absorbencies of each band into positive values originating from transition moments, which form average angles with the orientation direction (n) between 0° and 54.7° (magic angle), and negative ones corresponding to transition moments between 54.7° and 90°. In the *reducing-difference procedure*, the perpendicular spectrum multiplied by the parameter c, is subtracted from the parallel one and c is varied until at least one band or sets of bands are eliminated. The simultaneous disappearance of these bands in the *reduced* IR-LD spectrum (IR_p–cIR_s) obtained indicates co-linearity of the corresponding transition moments, thus yielding to information regarding the mutual disposition of the molecular fragments. This elimination method is carried out graphically using a subtraction procedure attached to the program for processing of IR spectra.

HPLC MS–MS measurements are made using TSQ 7000 (Thermo Electron Corporation) instrument under the conditions presented in Table 1. Two flows were used: (i) A–H_2O and 0.1% HCOOH and (ii) B–CH_3CN and 0.1% HCOOH.

The *FAB mass spectra* were recorded on a Fisons VG autospect instrument employing 3-nitrobenzylalcohol as matrix. The elemental analysis was carried out according to the standard procedures for C and H (as CO_2, and H_2O) and N (by the Dumas method). The thermogravimetric study was carried out using a Perkin-Elmer TGS2 instrument. The calorimetry was performed on a DSC-2C Perkin-Elmer apparatus under argon.

2.1.1. ESI mass spectrometry

A triple quadruple mass spectrometer (TSQ 7000 Thermo Electron, Dreieich, Germany) equipped with an ESI 2 source was used and operated with the following conditions: capillary temperature 180 °C; sheath gas 60 psi, corona 4.5 μA and spray voltage 4.5 kV. The sample was injected in the ion source by an autosampler (Surveyor) with a flow rate of 0.2 ml/min a pure acetonitrile. About 1 mg/ml of the sample was dissolved in aceto-

Table 1
HPLC-MS–MS conditions

N	t (min)	A (%)	B (%)	Rate (μl min^{-1})
0	0.00	100	0	200
1	3.00	100	0	200
2	8.00	65	35	200
3	9.00	0	100	200
4	14.00	0	100	200
5	14.50	100	0	200
6	20.00	100	0	200

nitrile. The data obtained was processed using an Excalibur 1.4 software.

^{1}H- and ^{13}C-*NMR measurements*, referred to sodium 3-(trimethylsilyl)-tetradeuteropropionate, were made at 298 K with a Bruker DRX-400 spectrometer using 5 mm tubes and D_2O as solvent.

Optimisation of the structure of Au(III)-complex of *H–Phe–Tyr–OH* was carried out by *density funclional theory* calculations (B3LYP) and Lanl2DZ (Au)/6-31+G(3df) (Cl, C, H) basis set [24,27] with polarization function alpha 0.2 and 1.2 (Au). The theoretical analysis was carried out using the Dalton 2.0 program package [28].

2.2. Synthesis

Au(III)-complex of *H–Phe–Tyr–OH*, [Au($C_{18}H_{18}N_2O_4$)Cl], was obtained by a mixing of 0.5670 g of $HAuCl_4 \times 3H_2O$ in 5 ml water to 5 ml of H_2O solution containing 0.2787 g of dipeptide at (metal to ligand) mole ratio of 1:2. After 15 days, the isolated yellow precipitate was filtered off, washed with water and dried over P_2O_5. Yield: 61%, mp 353 °C. (Found: C, 38.55; H, 3.25; N, 5.01; [Au($C_{18}H_{18}N_2O_4$)Cl] calcd.: C, 38.69; H, 3.25; N, 5.01%). TGV and DSC analysis in the range 300–500 K showed that no solvent was included in the complex.

The hydrogen squarate of *H–Phe–Tyr–OH* (*H_2Sq* × *H–Phe–Tyr–OH*), [$C_{22}H_{21}N_2O_8$], was obtained according the procedure: an aqueous solution of dipeptide *H–Phe–Tyr–O*H (5 ml, 0.3291 g) was mixed with 5 ml 0.1140 g squaric acid in same solvent at equimolar ratio 1:1. The white crystals are formed after 10 days and were filtered, washed with H_2O and dried at 298 K in air. (Found: C, 59.88; H, 4.80; N, 6.34; [$C_{22}H_{21}N_2O_8$] calcd.: C, 59.86; H, 4.80; N, 6.35%. Yield 78%). TGV and DSC analysis in the range 300–500 K showed that no solvent was included in the complex.

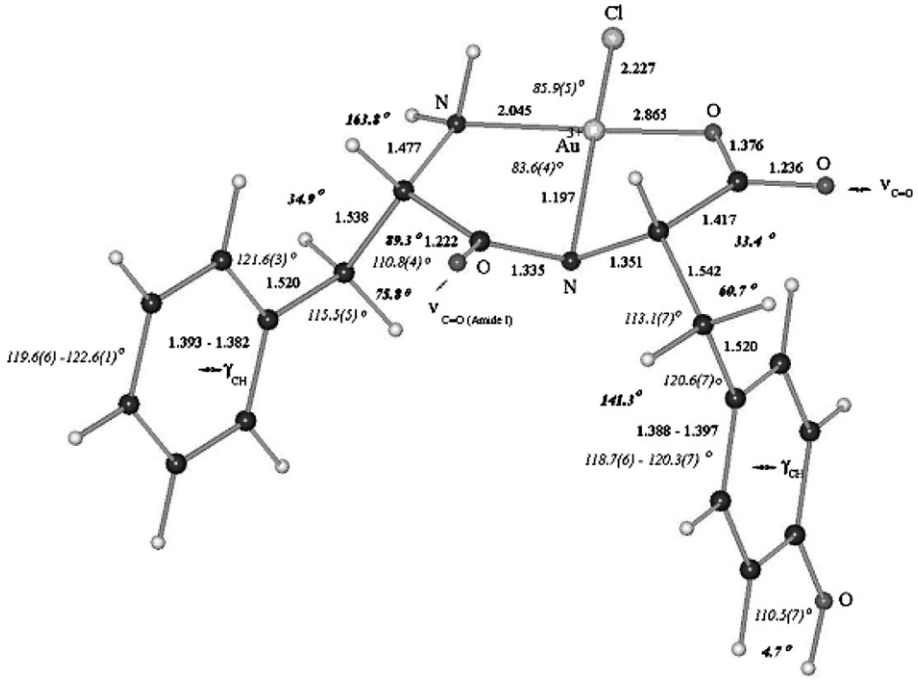
3. Results and discussion

3.1. Theoretical calculations

The predicted geometry parameters of Au(III)-complex of *H–Phe–Tyr–OH* are listed in Scheme 2 and are made in the basis of the experimental spectroscopic results about the way for coordination of metal center with dipeptide (see below). The predicted geometry assumed a co-linear orientation of following transition moments in the frame of the complex molecule: out-of-plane aromatic ones (11-γ_{CH} and 4-γ_{Ar} according Wilson notation [29]), typical for mono- and *para*-disubstituted benzene fragments and $\nu_{C=O}$ stretchingfrequency of carboxylic group. These results supported as well the conclusions obtained [30–32] about the application of DFT calculations at B3LYP and Lanl2DZ (Au)/6-31+G(3df) (Cl, C, H) with polarization function alpha 0.2 and 1.2 (Au) as far as the calculated bond length and angles are compared with crystallographic data about the known Au(III)-complexes with di- and tripeptides [33–36] and the values are not differ that 0.098 Å and 3.3(4)°. Furthermore, the shown geometry of the complex is confirmed from the linear polarized IR-data obtained and included in next part.

3.2. IR- and IR-LD data

The comparison of IR-spectral characteristics of Au(III)-complex and hydrogensquarate of *H–Phe–Tyr–OH*



Scheme 2. Optimized geometry of the Au(III)-complex of *H–Phe–Tyr–OH*.

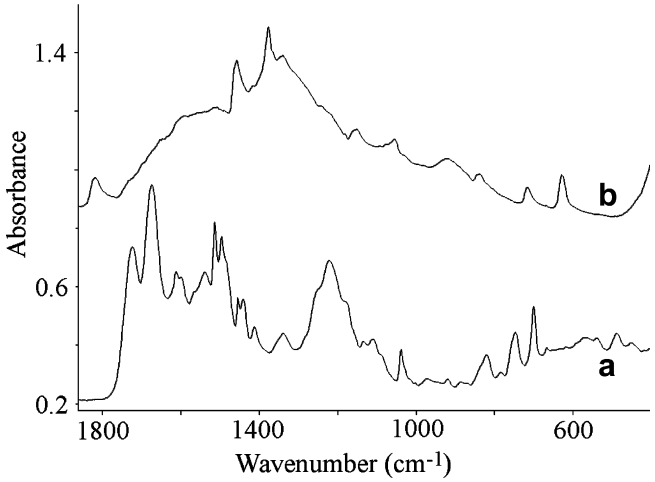


Fig. 1. Solid-state IR-spectra of *H–Phe–Tyr–OH* complex with Au(III) (a) and its hydrogensquarate (b).

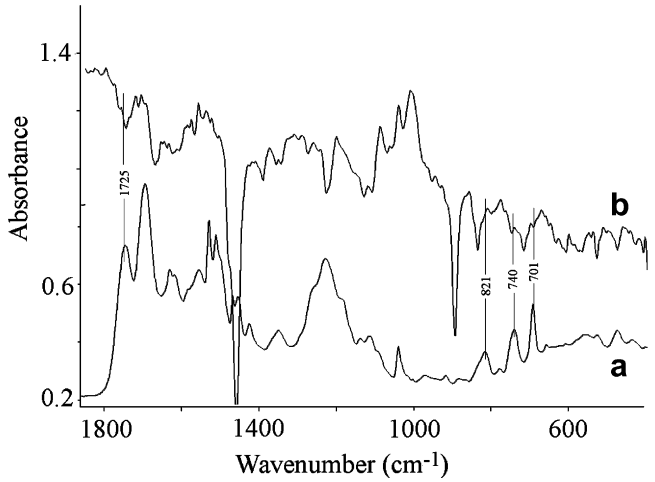


Fig. 2. Nonpolarized IR (a) and reduced IR-LD spectrum (b) of Au(III)-complex of *H–Phe–Tyr–OH* after elimination of the peak at 1725 cm^{-1}.

is made towards the known theoretical and experimental data about pure dipeptide and its hydrochloride salt [37]. The main characteristic IR-bands are listed as: (i) *H–Phe–Tyr–OH*: 3220 cm^{-1} (ν_{NH}), 1681 cm^{-1} (δ^{as}_{NH3+}), 1670 cm^{-1} (amide I), 1630 cm^{-1} ($8a_{(Phe)}$), 1614 cm^{-1} ($8a_{(Tyr)}$), 1594 cm^{-1} ($8b_{(Phe)}$), 1585 cm^{-1} ($8b_{(Tyr)}$), 1564 cm^{-1} ($19a_{(Phe)}$), 1554 cm^{-1} (amide II), 1525 cm^{-1} (ν^{as}_{COO-}), 1511 cm^{-1} ($19a_{(Tyr)}$); (ii) *H–Phe–Tyr–OH hydrochloride salt*: 3160 cm^{-1} (ν_{NH}), 1731 cm^{-1} ($\nu_{C=O}$, COOH group) 1656 cm^{-1} (δ^{as}_{NH3+}), 1650 cm^{-1} (amide I), 1612 cm^{-1} (8a), 1593 cm^{-1} ($8b_{(Phe)}$), 1587 cm^{-1} ($8b_{(Tyr)}$), 1600 cm^{-1} (amide II), 1514 cm^{-1} ($19a_{(Tyr)}$), 1498 cm^{-1} ($19a_{(Phe)}$).

The comparison with neutral peptide and its Au(III)-complex indicated the following main differences: (i) the ν_{NH} and amide II peaks are disappeared after complexation (Fig. 1a). (ii) the pairs of ν^{as}_{COO-} and ν^{s}_{COO-} maxima are also absent in the IR-spectrum of the complex and a new band at 1722 cm^{-1} is at hand belonging to $\nu_{C=O}$; (iii) the new peaks at 3386 cm^{-1}, 3205 cm^{-1}, 3070 cm^{-1} and 1658 cm^{-1} could be explained with ν^{as}_{NH2}, Fermi-resonance splitted ν^{s}_{NH2} and δ_{NH2} stretching and bending modes. This assignment is supported by the disappearance of NH_3^+ characteristic bands, typical for neutral dipeptide. These data assumed a tridentate coordination of *H–Phe–Tyr–OH* through its $–NH_2$, $–COO^-$ and deprotonated –NH (amide) groups. Other characteristic IR-bands of Au(III)-complex are: 1675 cm^{-1} (amide I), 1627 cm^{-1} ($8a_{(Phe)}$), 1614 cm^{-1} ($8a_{(Tyr)}$), 1596 cm^{-1} ($8b_{(Phe)}$), 1587 cm^{-1} ($8b_{(Tyr)}$), 1566 cm^{-1} ($19a_{(Phe)}$), 1513 cm^{-1} ($19a_{(Tyr)}$), 840 cm^{-1} (4-$\gamma_{Ar(Tyr)}$), 738 cm^{-1} (11-$\gamma_{Ar(Phe)}$) and 701 cm^{-1} (4-$\gamma_{Ar(Phe)}$).

The complicated IR-spectrum of hydrogensquarate of *H–Phe–Tyr–OH* (Fig. 1b) due to the strong intermolecular interactions between dipeptide and HSq^- ions required a preliminary deconvolution and curve-fitting for obtaining the number of maxima and their position: 3340 cm^{-1} (ν_{NH}), 1740 cm^{-1} ($\nu_{C=O}$, COOH group) 1669 cm^{-1} (δ^{as}_{NH3+}), 1645 cm^{-1} (amide I), 1613 cm^{-1} (8a), 1598 cm^{-1} ($8b_{(Phe)}$), 1590 cm^{-1} ($8b_{(Tyr)}$), 1523 cm^{-1} (Amide II), 1516 cm^{-1} ($19a_{(Tyr)}$), 1500 cm^{-1} ($19a_{(Phe)}$). Like in hydrochloride salt [37] the interactions with squaric acid leads to protonation of COO^- group and disappearance of ν^{as}_{COO-} and ν^{s}_{COO-} maxima. The IR-spectrum of hydrogensquarate shows as well series of IR-peaks characteristic for HSq^- ion at 1818 cm^{-1}, 1703 cm^{-1} and 1600 cm^{-1} assigned to combination of ν_{C-O}, ν_{C-C} and $\nu_{C=C}$ modes. The peaks positions are typical for the other obtained hydrogensquarates of peptides and amino-acid amides [35].

Polarized IR-LD data of Au(III)-complex leads to following conclusions based on the applied reducing-difference procedure. The elimination of carboxylic $\nu_{C=O}$ stretching peak at 1725 cm^{-1} resulted to disappearance of out-of-plane modes characteristic for mono- and *para*-disubstituted benzene fragments (Fig. 2b) at 821 cm^{-1} (11-$\gamma_{Ar(Tyr)}$), 748 cm^{-1} (11-$\gamma_{Ar(Phe)}$) and 701 cm^{-1} (4-$\gamma_{Ar(Phe)}$). This result indicated a co-linear orientation of corresponding transition moment, which is realized in the frame of the shown structure in Scheme 2. In parallel during the last procedure the peak of amide I at 1675 cm^{-1} is observed also supported the presented structure due to the mutual cross-oriented transition moments of both $\nu_{C=O}$ modes closing an torsion angle of 65.7°.

3.3. ^1H- and ^{13}C-NMR data

The nuclear magnetic resonance spectra Au(III)-complex and hydrogensquarate of *H–Phe–Tyr–OH* are compared with zwitterion form of dipeptide [38–41]. The α-(1**H**) and β-(2**H**) protons in *Phe*-residues are observed generally about 4.50 and 3.00 ppm as doublets *dd* and *2dd*, respectively. The aromatic protons (5**H**) are obtained over 7.00 ppm as multiplet (*m*). The *Tyr*-side chain shown signals about 3.00 ppm (1**H**, dd, β-*Tyr*), 3.30 ppm (m, 1**H**, β–*Tyr*), 4.90 ppm (dd, 1**H**, α-**Tyr**), 5.83 ppm (d, 2**H**), 6.51 (d, 1**H**), 6.70 ppm (d, 1**H**), respectively. The corresponding ^{13}C-NMR chemical shifts are about 35.00 ($\mathbf{C}H_2$, *Phe*), 55.70 (**C**H, *Phe*),

129.35, 131.23, 131.2 (*Phe*), 38.9 (β-*Tyr*), 55.0 (α-Tyr), 83.5, 98.0, 97.5, 100.1 (*Tyr*), 166.0 (**C**OH, *Tyr*), respectively, The signals about 165.00 ppm and 175.00 ppm correspond to $\mathbf{C}OO^-$ and **C**ONH, respectively.

The complexation with Au(III) leads to following differences in the ^{1}H- and ^{13}C-NMR spectra of the dipeptide. The β-*Phe* (2**H**, dd) and β-**Tyr** (m, dd, 1**H**) signals are downfield shifted and overlapped about 4.50 ppm. The α-*Phe* and α-*Tyr* dd (1**H**) signals are shifted as well and are observed at 5.20 ppm and 5.35 ppm. The other signals are practically insignificant shifted and are observed in the 6.00–7.50 ppm range. These data assumed a tridentate coordination of dipeptide with Au(III) center through $-NH_2$, $-COO^-$ and $-N^-$of amide group. The ^{13}C-NMR data of Au(III)-complexes are 37.5 (β-*Phe*), 56.0 (α-*Phe*), 130.5, 131.0, 135.0 (*Phe*), 38.5 (β-*Tyr*), 55.2 (α-*Tyr*), 125.5, 128.0, 128.9, 129, 5 (*Tyr*), 159.0 (**C**OH, *Tyr*), 169.5 ppm ($\mathbf{C}OO^-$) and 172.5 (**C**ONH), respectively.

The ^{1}H-NMR data of hydrogensquarate of *H–Phe–Tyr–OH* are: (i) The chemical shifts of β-*Phe* (2**H**, dd), α-*Phe* (dd, 1**H**) and aromatic 5**H** are practical unaffected after the protonation of COO- group in zwitterion dipeptide; (ii) β–**Tyr** (m, dd, 1**H**) and α–*Tyr* dd (1**H**) signals are downfield shifted with about 1.00 ppm and 4. ppm, respectively. The aromatic signals in the 6.00–7.50 ppm range are practically insignificant. These data correlated well with known ones about the protonated forms of tyrosine and phenylalanine containing dipeptides [42]. However, the ^{13}C-NMR data of hydrogensquarate are significant differ than the neutral dipeptide one due to an observation of four new signals at 184.6, 180.9, 176.9, 170.0 ppm, belonging to HSq^- ion [43]. The dipeptide signals in the salt are 39.4 (β-*Phe*), 56.9 (α-*Phe*), 130.0, 132.0, 135.5 (*Phe*), 37.5 (β, *Tyr*), 59.2 (α-*Tyr*), 125.9, 128.9, 131.8, 132, 5 (*Tyr*), 159.7 (**C**OH, *Tyr*), 175.5 ppm (**C**OOH) and 172.5 (**C**ONH), respectively.

3.4. ESI-MS and HPLC-MS–MS data

The most intense peak in the FAB mass spectrum of the Au(III)-complex is at 559.2 *m*/*z*, corresponding to the single charged $[C_{18}H_{19}N_2O_4AuCl]^+$ ion with molecular weight 559.7.

The ESI-MS spectrum of hydrogensquarate is given in Fig. 3. The most intensive peak is at *m*/*z* 357.0. As far as the molecule weight of protonated *H–Phe–Tyr–OH*, $[C_{18}H_{20}O_4N_2]^+$, is 329.12, the signals should be corresponds to an NH_4^+ adduct with dipeptide. The peak at 467.08 could be assigned to Na^+ adduct with *H–Phe–Tyr–OH*$\cdots$$HSq^-$ specie, which have a molecule weight of 443.01. It is well-known that the Na^+ and NH_4^+ adducts are typical for ESI-MS and for that reason for the analysis of peptides and their derivatives is preferable a combination of HPLC-MS–MS determination [44–48]. The HPLC separation of system studied is presented in Fig. 4A as a dependence of relative abundance *vs*. time (*t*). Two peaks are observed at $t = 1.94$ min and $t = 11.51$ min. The MS data of first one given a peak at *m*/*z* 329.2, which correlated with the molecule weigh of protonated peptide with formula $[C_{18}H_{20}O_4N_2]^+$ (Fig. 4B). The maximum at 657.4 belongs to dimmers of the dipeptide studied. The second peak in Fig. 4B corresponds to molecule species with *m*/*z* 119.9 corresponds to protonated hydrogensquarate. The

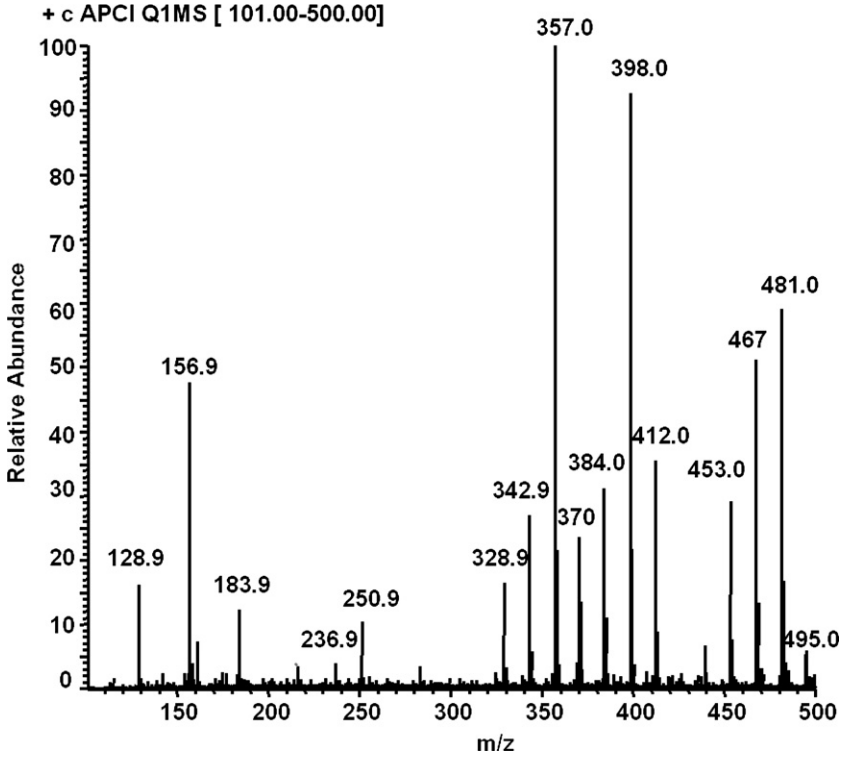


Fig. 3. ESI mass-spectrum of $H_2Sq \times$ *H–Phe–Tyr–OH*.

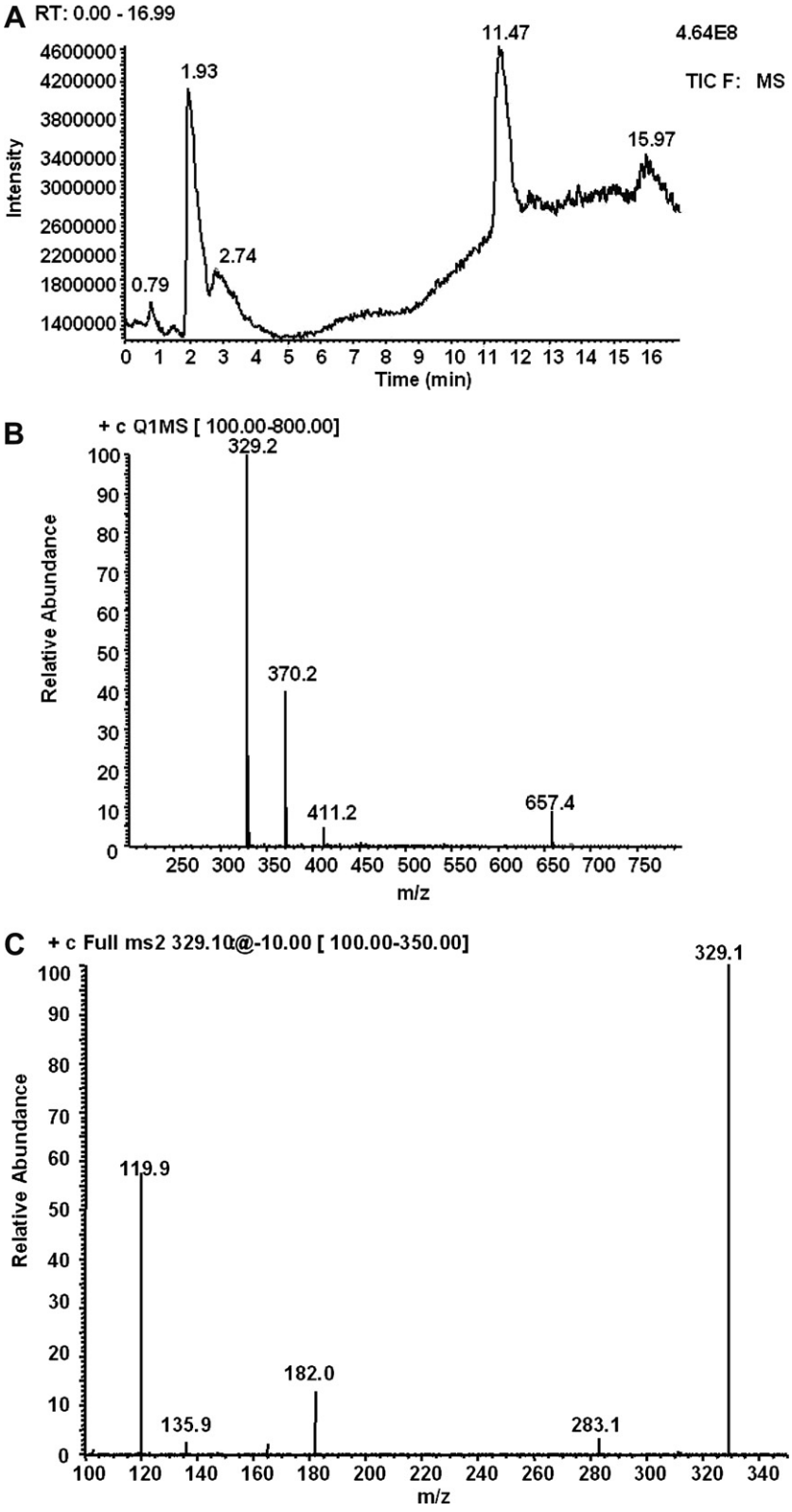


Fig. 4. HPLC-MS–MS spectra of $H_2Sq \times H$–*Phe–Tyr–OH*.

MS–MS spectrum given in Fig. 4C gives a peak at m/z 329.1 exactly given the molecule mass of the dipeptide studied and confirmed the synthesis of hydrogensquarate salt of *H–Phe–Tyr–OH*.

4. Conclusions

On the basis of solid-state IR-LD spectroscopy, ^{1}H- and ^{13}C-NMR, ESI-MS, HPLC-MS–MS, FAB-MS, TGS and

DSC as well as by DFT calculations at B3LYP level of and Lanl2DZ (Au)/6-31+G(3df) (Cl, C, H) basis set using polarization function alpha 0.2 and 1.2 (Au) the following essential conclusions can be drown: (i) A mononuclear Au(III)- complex of *H–Phe–Tyr–OH* has been synthesised and is characterized with a tridentate coordination of dipeptide through its $–NH_2$, $–COO^-$ and $–N^-$-groups. One Cl^- is attached as a terminal ligand in four position to metal ion, forming a planar geometry of the Au(III) center; (ii) hydrogensquarte of *H-Phe–Tyr–OH* has been obtained consists in positive charged dipeptide moiety and negative one hydrogensquarate anion (HSq^-) stabilizing by strong intermolecular hydrogen bonds; (iii) A precise vibrational assignment of both system studied has been obtained by means of solid-state IR-LD spectroscopy of oriented samples in nematic liquid crystal suspension; (iv) The comparison with IR-spectroscopic and ^1H- and ^{13}C-NMR data as well as with all mass spectral ones indicated the same type of Au(III) coordination with dipeptide both in solid-state and in solution.

Acknowledgements

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