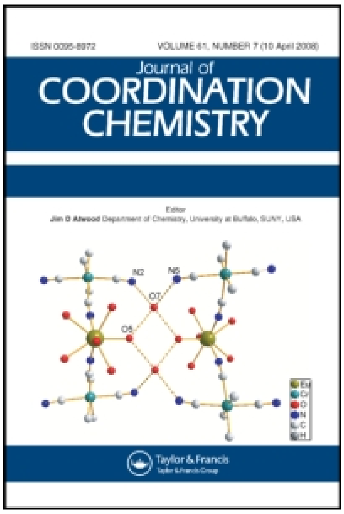

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Solid-state linear-dichroic infrared spectroscopic analysis of the dipeptide *S*-Phe-*S*-Phe and its mononuclear Au(III) complex

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To cite this Article Ivanova, Bojidarka B.(2005) 'Solid-state linear-dichroic infrared spectroscopic analysis of the dipeptide *S*-Phe-*S*-Phe and its mononuclear Au(III) complex', Journal of Coordination Chemistry, 58: 7, 587 — 593
To link to this Article: DOI: 10.1080/00958970500039033
URL: http://dx.doi.org/10.1080/00958970500039033

Journal of Coordination Chemistry
Vol. 58, No. 7, 10 May 2005, 587–593

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Solid-state linear-dichroic infrared spectroscopic analysis of the dipeptide *S*-Phe–*S*-Phe and its mononuclear Au(III) complex

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(*Received in final form 2 November 2004*)

Interaction between the *S*-Phe–*S*-Phe dipeptide (PP) and Au(III) leads to the formation of a yellow complex, [Au(PP)Cl_3]Cl (**1**), with monodentate coordination of the dipeptide with Au(III) through one O atom of the COO^- group. Three Cl^- anions bond to the metal center as terminal ligands. The structure of **1** was obtained by comparative solid-state linear-dichroic infrared (LD-IR) spectroscopic analysis of a solid sample and the pure dipeptide *S*-Phe–*S*-Phe, both oriented in a nematic liquid crystal suspension.

Keywords: LD-IR analysis; Gold(III); Dipeptide; *S*-Phe–*S*-Phe

1. Introduction

Investigations of potential antitumor agents have mainly concerned studies of Au(III) and Pt(II) complexes of amines, amino acids and peptides [1–3]. An understanding of the coordination behavior of these compounds has led to clarification of the *in vivo* mechanism of metal–DNA interactions in the cell [4, 5]. Infrared spectroscopic investigations of peptide systems however, are complicated by the presence of more than one peptide bond, leading to complex spectroscopic properties. In addition, free peptide bond rotation leads to various conformers possessing different biological activities.

For these reasons, a linear-dichroic infrared (LD-IR) spectroscopic characterization of the dipeptide *S*-Phe–*S*-Phe (scheme 1) and its Au(III) complex has been carried out to illustrate the LD-IR spectral technique, first reported with respect to Cu(I)-homocysteine [6], and based on the polarized spectra of solid-state samples oriented in a nematic liquid crystal suspension. Development of the technique permits study of complexation sites and coordination modes of compounds, as is the case for the Au(III)–*S*-Phe–*S*-Phe complex, the object of the present article.

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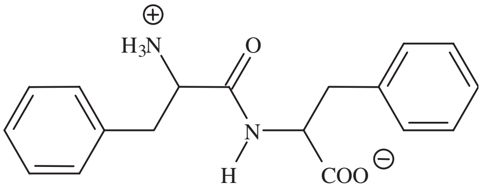
Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/00958970500039033



Scheme 1. *S*-Phe–*S*-Phe.

2. Experimental

2.1. *Synthesis*

[Au(PP)Cl_3]Cl (**1**) was obtained by the addition of 0.1705 g of $HAuCl_4 \cdot 3H_2O$ in 10 cm^3 of H_2O to 10 cm^3 of a methanol solution containing 0.4055 g of *S*-Phe–*S*-Phe (PP; mol ratio Au : PP = 1 : 1). After 2 weeks, the yellow precipitate that had formed was filtered off, washed with methanol and dried over P_2O_5. Yield: 66%, m.p. 289°C. Anal. Calcd for [Au^{III}(PP)Cl_3]Cl(%): C, 33.20; H, 3.10; N, 4.30; Cl, 21.78. Found: C, 33.00; H, 2.97; N, 4.30; Cl, 21.81. The most intense peak in the mass spectrum of **1** is at 615.5 *m*/*z*, corresponding to the singly-charged $[C_{18}H_{20}N_2O_3Cl_3Au]^+$ ion with molecular weight 615.7. Thermogravimetric analysis in the range 350–500 K showed that no solvent was included in the complex.

2.2. *Analysis*

Conventional and linear-dichroic IR spectra (4000–400 cm^{-1} region, 150 scans, 4 cm^{-1} resolution) were recorded on a Bomem–Michelson 100 FTIR spectrometer, equipped with a Perkin Elmer wire-grid polarizer. A 4-cyano-4′-alkylbicyclohexyl mixture (ZLI-1695, Merck) was used for orientation of the compounds. The LD-IR technique for solid-state orientation as a suspension in a nematic mesophase has been described previously [6–8]. The co-call reduced procedure for polarized spectra interpretation was adopted [6, 9, 10].

FAB mass spectra were measured on a Fisons VG Autospect instrument with 3-nitronenzyl alcohol as matrix. Elemental analysis was performed according to classical methods; C and H were determined as CO_2 and H_2O, N by Duma's method and chlorine by titration with $Hg(NO_3)_2$ after wet digestion of a sample. Thermogravimetric measurements were performed using a Perkin-Elmer TGS-2 system.

3. Results and discussion

3.1. *IR spectroscopic analysis of S-Phe–S-Phe*

Nonpolarized and difference IR spectra of *S*-Phe–*S*-Phe in ZLI 1695 suspension (figure 1) are characterized by 3255 cm^{-1} (ν_{NH}) and 1687 cm^{-1} ($\nu_{C=O}$) peaks of the peptide bond [11–14]. As is well known [15], in the solid state *S*-Phe–*S*-Phe exists in the zwitterionic form and therefore the multiple band between 3400 and 2600 cm^{-1} is assigned to $\nu_{NH_3^+}$ stretching vibrations. Eliminated 1621 cm^{-1} ($\delta^{d}_{NH_3^+}$), 1558 cm^{-1} (Amide II) and positive 1606 cm^{-1} (8a), 1579 cm^{-1} (8b, B_2), 1506 cm^{-1} (19a)

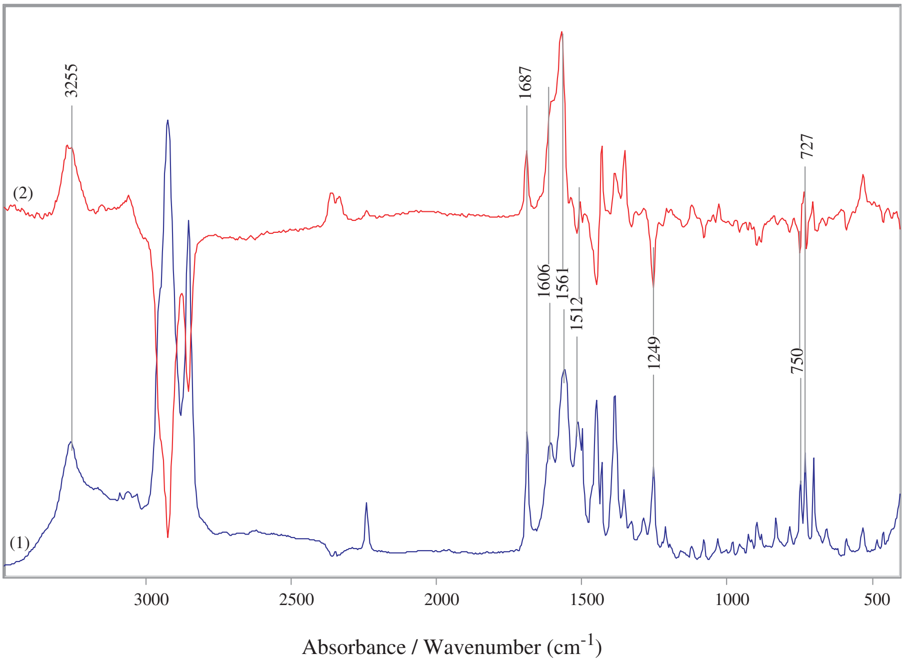
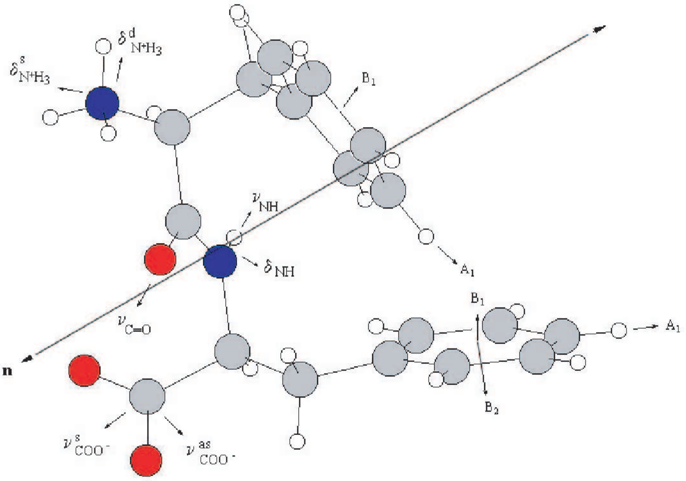


Figure 1. Nonpolarized (1) and difference LD-IR (2) spectra of *S*-Phe–*S*-Phe in ZLI 1695 suspension.

and 1430 cm^{-1} $\nu^{s}{}_{COO^-}$ peaks are presented in the spectrum of figure 2. The negatively oriented maxima at 1546, 1517 and 1496 cm^{-1} belong to $\delta^{s}{}_{NH_3^+}$, $\nu^{as}{}_{COO^-}$ and 8a modes, respectively. The 750–670 cm^{-1} region shows A_1 and B_1 modes for both the benzene rings with the following orientations: the negative 750, 732 and 701 cm^{-1} peaks and the positive 742, 732 and 705 cm^{-1} peaks correspond to 11 γ_{-CH} o.p., 12 A_1 i.p. and 4 B_1 o.p. modes. Pairs of maxima were obtained in the nonpolarized spectra using curve-fitting procedures (figure 3). Collinear orientation of A_1 i.p. and B_1 o.p. (scheme 1) in the frame of one benzene ring is impossible and the results indicate orientation of both the phenyl fragments as shown in scheme 2. A collinear disposition of NH and C=O bonds in the peptide fragment with the liquid crystal orientation direction is assumed in view of the peak orientation in the difference spectrum of *S*-Phe–*S*-Phe.

The stepwise reduction procedure applied confirmed the conformation shown in scheme 2. With elimination of the 1689 cm^{-1} peak (figure 2), disappearance of ν_{NH} at 3255 cm^{-1} and the 1621 cm^{-1} peak of $\delta^{d}{}_{NH_3^+}$ is observed, thus indicating a *trans*, near to planar disposition of the peptide bond and collinearity of the corresponding transition moments. Reduction of the 1430 cm^{-1} peak and disappearance of the 742, 732 and 705 cm^{-1} peaks was also observed (figure 3). Elimination of the 750 cm^{-1} peak (figure 2) led to the disappearance of the 1519 and 1498 cm^{-1} maxima, showing the collinear transition moments of B_1 o.p., A_1 i.p. $\nu^{as}{}_{COO^-}$ modes, illustrated in scheme 2. Corresponding B_1 and A_1 modes in the 750–680 cm^{-1} region for the second phenyl fragment are observed as a result of the last reduction (figure 3). Comparison of the indicated geometry of *S*-Phe–*S*-Phe derived from IR-LD spectra with the known conformation obtained by X-ray structural methods [7] shows good correlation.



Scheme 2.

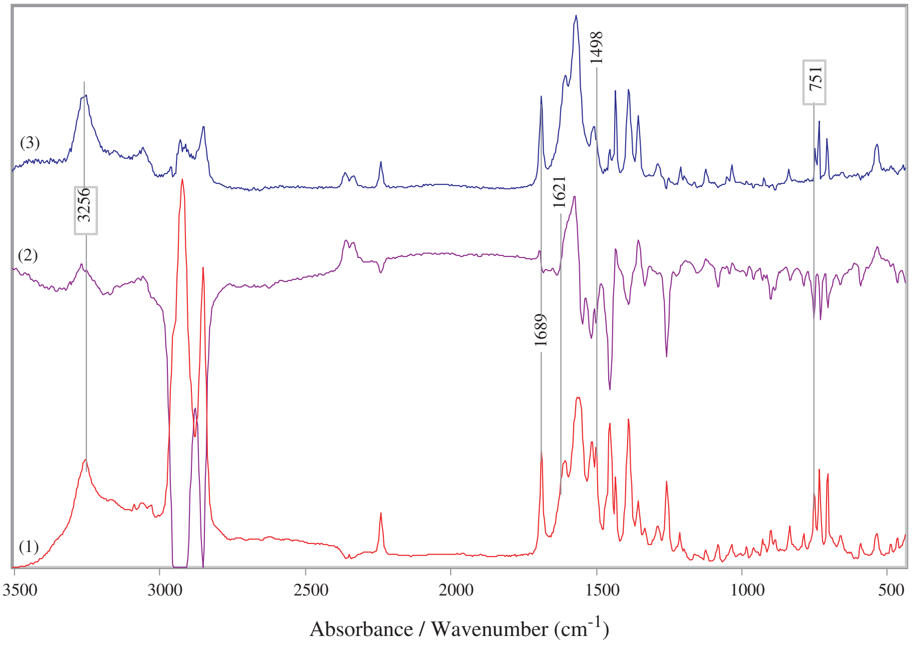


Figure 2. Nonpolarized (1) and reduced LD-IR spectra of *S*-Phe–*S*-Phe after elimination of the absorption maxima at 1687 (2) and 750 cm^{-1} (3).

3.2. *IR spectroscopic analysis of [Au(PP)Cl$_3$]Cl*

A comparative LD-IR analysis of solid *S*-Phe–*S*-Phe and its Au(III) adduct led to the following: the solid-state spectrum of **1** in the 3500–3000 cm^{-1} region is characterized by a high-frequency shift of the ν_{NH} peak from 3255 cm^{-1} in pure *S*-Phe–*S*-Phe

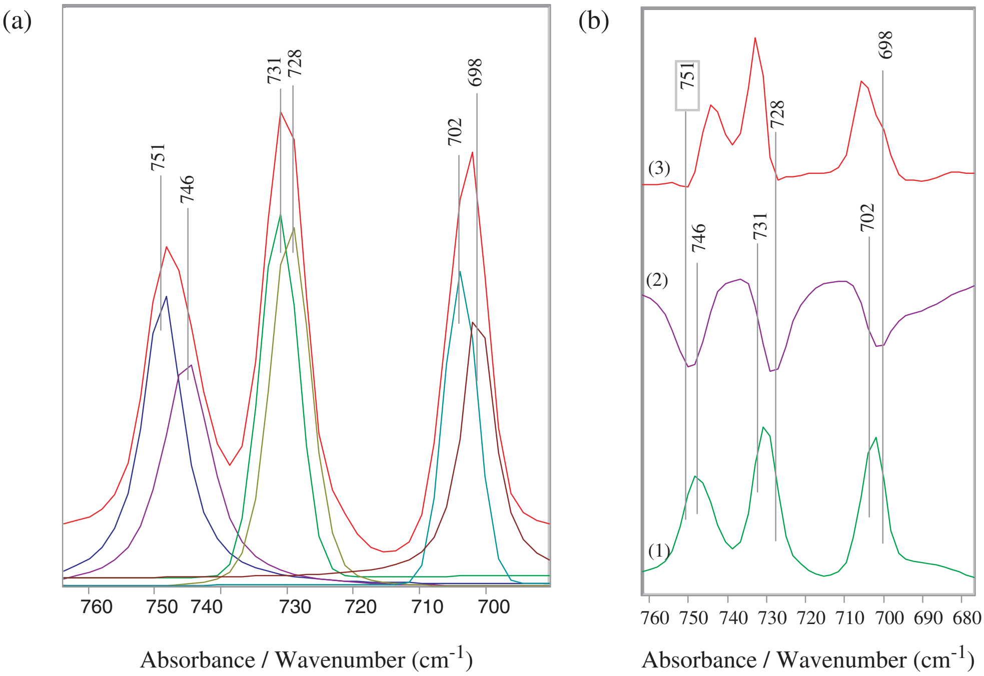


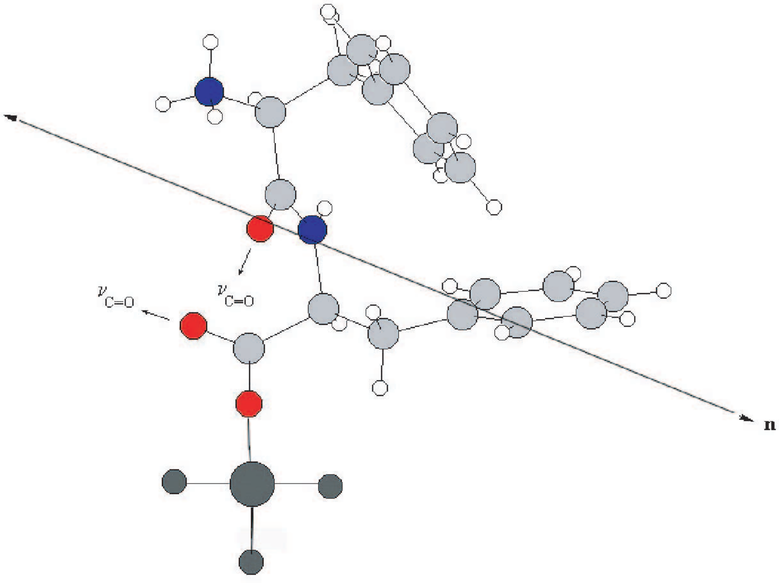
Figure 3. (a) The 760–680 cm^{-1} deconvoluted, nonpolarized spectrum of *S*-Phe–*S*-Phe; (b) 760–680 cm^{-1} nonpolarized (1) and reduced LD-IR spectra of *S*-Phe–*S*-Phe after elimination of the 1687 (2) and 750 cm^{-1} (3) peaks.

to 3288 cm^{-1}. However, the broad multiple band at 3600–2400 cm^{-1} and the maxima at 1621 and 1546 cm^{-1} in the spectrum of the complex are present, indicating the maintenance of the protonated amino group. A new absorption maximum at 1666 cm^{-1} and the disappearance of the 1517 and 1430 cm^{-1} peaks, characteristic of COO$^-$, are noted, indicating Au(III)–O bond formation with the COO$^-$ group of PP (figure 4). The difference spectrum of **1** shows negatively oriented $\nu_{C=O}$ peaks at 1687 cm^{-1} (peptide bond) and a positive new peak at 1666 cm^{-1} assigned to $\nu_{C=O}$ of the COO–Au(III) fragment (figure 4). The latter is typical of amino acid and peptide complexes with monodentate coordination through one O atom. In the 750–680 cm^{-1} region, a series of maxima involving B_1 and A_1 phenyl modes at 767 and 703 cm^{-1} (both positive) and at 742 and 700 cm^{-1} (negative oriented) is also observed, indicating orientation of the complex molecule in the liquid crystal direction (**n**) shown in scheme 3.

With elimination of the second 1666 cm^{-1} peak, the disappearance of the 1546 ($\delta^s_{NH_3^+}$), 765 and 725 cm^{-1} peaks was also established (figure 5), confirming the conformer in scheme 3. The geometry of **1** predicted by LD-IR analysis is similar to those obtained for other Au(III) complexes of dipeptides [16–18].

3.3. *Conclusions*

Solid-state LD-IR studies of *S*-Phe–*S*-Phe and [Au(PP)Cl$_3$]Cl, both orientated in a nematic liquid crystal suspension, with a view to stereochemical characterization



Scheme 3.

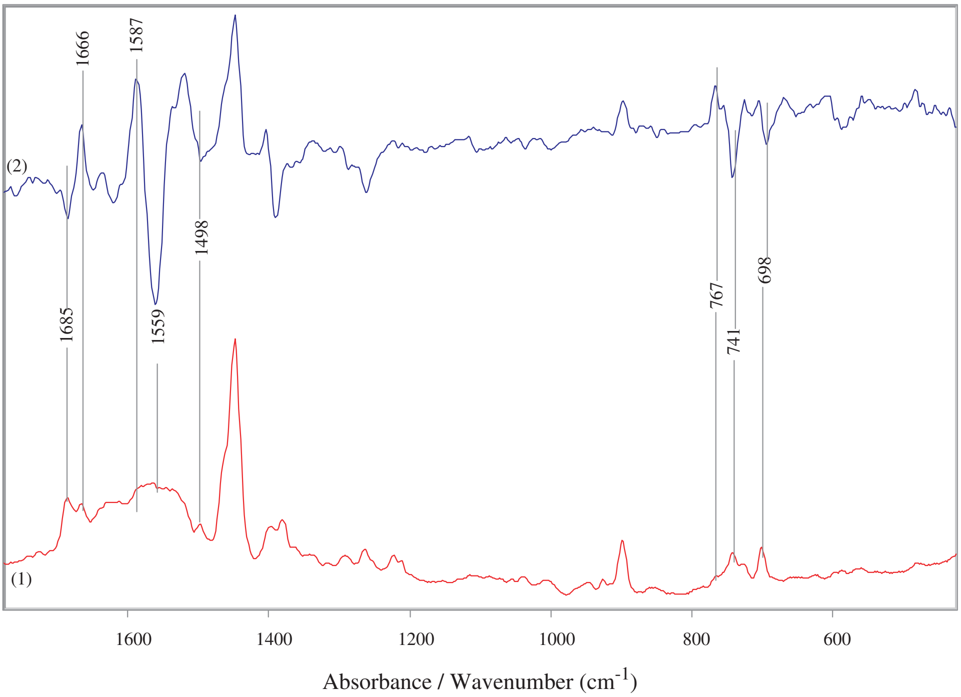


Figure 4. The 1750–400 cm^{-1} nonpolarized (1) and difference LD-IR (2) spectra of [Au(PP)Cl_2]Cl in ZLI 1695 suspension.

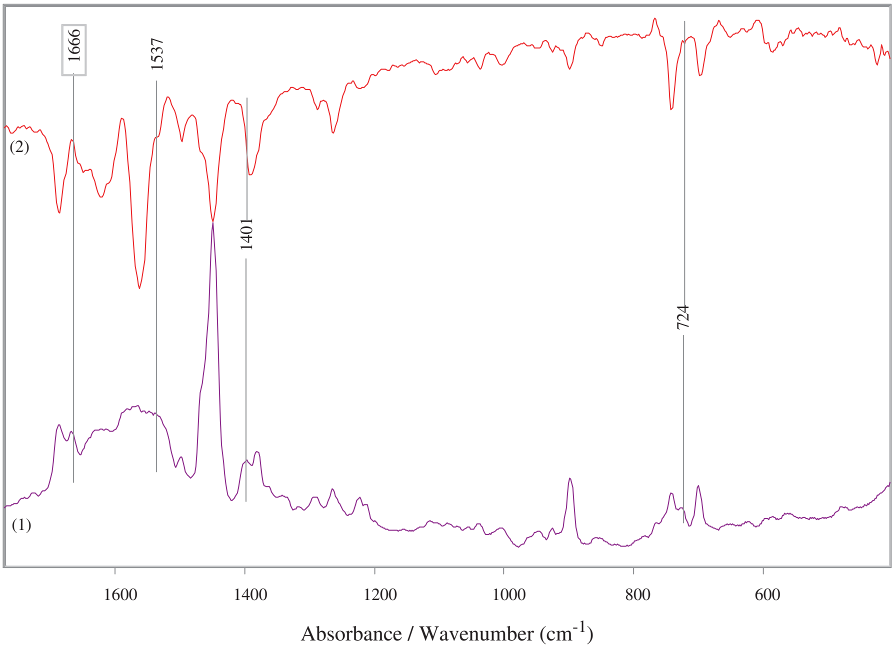


Figure 5. The 1750–400 cm^{-1} nonpolarized (1) and reduced LD-IR spectra of $[Au(PP)Cl_2]Cl$ after elimination of the 1666 cm^{-1} peak (2).

of both the dipeptide and its Au(III) adduct were carried out. The results indicate the formation of an Au(III)–O bond through an O-atom of the COO^- fragment of the dipeptide in the complex. In addition, vibrational assignment of the ligand and the complex revealed the nature of the stable conformers in the solid state.

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