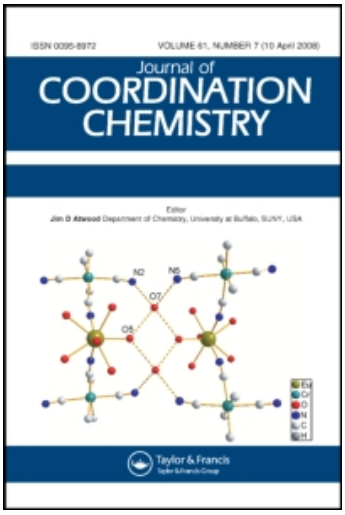

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Linear-dichroic infrared and NMR spectroscopic analysis of an Au(III) complex of glycylmethioninylglycine

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Linear-dichroic infrared and NMR spectroscopic analysis of an Au(III) complex of glycylmethioninylglycine

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A solid state, linear dichroic IR analysis of a mononuclear Au(III) complex of the tripeptide glycylmethioninylglycine (GlyMetGly) oriented in a nematic liquid crystal has been carried out. Structural results are compared with ^{1}H and ^{13}C NMR data. The ligand coordinates to Au(III) as a tridentate in $[Au(C_9H_{17}N_3O_4S)Cl]Cl_2$, binding through S, and the N- and O-atoms of neighbouring CONH– and COO^- groups. The fourth position is occupied by a terminal Cl^- ligand.

Keywords: GlyMetGly; Tripeptide; Gold(III); IR-LD analysis; NMR

1. Introduction

A full understanding of the *in vivo* mechanism and mode of coordination of Pt(II) and Au(III) with DNA requires a systematic investigation of their coordination with methionine-containing di- and tripeptides [1–3]. The potential antitumor action of certain Pt(II) and Au(III) complexes of peptides has prompted additional structural and spectroscopic studies [4–6]. For these reasons, the present work deals with the structural and spectroscopic characterization of an Au(III) complex of GlyMetGly (scheme 1). The complex is amorphous and thus its structure cannot be determined by X-ray diffraction methods. Therefore, an IR-LDs analysis of the solid as a nematic liquid crystal suspension, first demonstrated in [7], was carried out. Data obtained are confirmed by NMR measurements. The results obtained will be of use for the structural characterization of complexes of similar di- and tripeptides.

2. Experimental

2.1. *Materials and methods*

GlyMetGly was purchased from Bachem and $HAuCl_4 \cdot 3H_2O$ from Acros Organics. Conventional (KBr pellets) and IR-LD spectra were recorded between 4000 and

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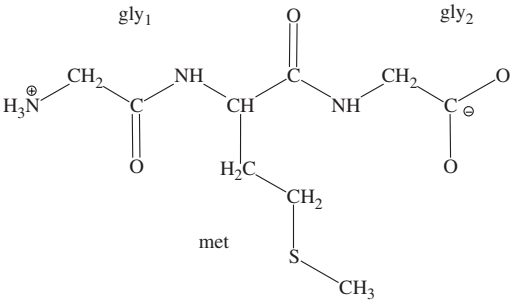


Scheme 1. Chemical formula of tripeptide Gly-Met-Gly.

$400\,cm^{-1}$ on a Bomem-Michelson 100 FTIR-spectrophotometer equipped with a Perkin-Elmer wire-grid polarizer. Some 150 scans were performed for each spectrum, with a resolution of $4\,cm^{-1}$. A 4-cyano-4′-alkylbicyclohexyl mixture (ZLI-1695, Merck) was used for orientation of the solid sample as a nematic liquid crystal suspension [6–8]. Its IR spectrum makes it possible to record guest-compound bands over the whole $4000–400\,cm^{-1}$ range. The effective orientation of the solid sample was achieved by means of a procedure described earlier [6–8]. The difference-reduction procedure for polarized spectra interpretation consists of subtraction of the perpendicular spectrum (IRs), resulting from the 90° angle between the polarized light beam electric vector and the orientation of the sample, from the parallel one (IRp) obtained with a co-linear orientation. The recorded difference (IRp-IRs) spectrum divides the corresponding parallel (Ap) and perpendicular (As) integrated absorbances of each band into positives, originating from transition moments which form an average angle with the orientation direction (n) between 0 and 54.7° (magic angle), and negative ones, corresponding to transition moments between 54.7 and 90° [9–12]. As a next step, the perpendicular spectrum multiplied by the parameter c, is subtracted from the parallel one and c varied until a band or set of bands is eliminated. The simultaneous disappearance of these bands in *the reduced* IR-LD spectrum indicates co-linearity of the corresponding transition moments, thus giving rise to information regarding the mutual disposition of molecular fragments.

^{1}H and ^{13}C NMR measurements, referenced to sodium 3-(trimethylsylyl)-tetradeuteriopropionate, were made at 298 K with a Bruker DRX-400 spectrometer using 5 mm tubes and D_2O as solvent. The elemental analysis was performed according to classical methods: C and H as CO_2 and H_2O, N through Duma's method, chlorine by titration with $Hg(NO_3)_2$ after wet digestion. The molecular weight was determined using FAB MS, measured on a Fusion VG Autospect instrument employing 3-nitrobenzylalchohol as matrix.

2.2. *Synthesis*

A solution of $HAuCl_4 \cdot 3H_2O$ (196.4 mg) in methanol ($5\,cm^3$) was added to a solution of the tripeptide (165.89 mg) in the same solvent ($5\,cm^3$). Dilute aqueous NaOH was added at mol ratio of $Au : L : NaOH = 1 : 1 : 1$. The yellow precipitate that formed during 15 days was filtered off, washed with methanol and dried on air at 298 K. Yield: 65%. Anal. Calcd for $[AuCl(C_9H_{17}N_3O_4S)]Cl_2$ (%): C, 19.08; H, 3.02; N, 7.42; Cl, 18.77.

Found: C, 19.10; H, 3.05; N, 7.43; Cl, 18.75. The most intense signal in FAB MS is at m/z 495.5, corresponding to $[Au(C_9H_{17}N_3O_4S)Cl]^+$. The data indicate a metal to ligand ratio of 1 : 1.

3. Results and discussion

3.1. *IR spectroscopy*

In IR spectra of both GlyMetGly [13] and its Au(III) complex (figure 1), a broad multiplet band between 3380 and 3000 cm^{-1}, corresponding to $\nu_{NH_3^+}$ is observed, indicating the presence of the NH_3^+-group in the complex. The observation of two maxima at 3284 and 3277 cm^{-1}, suggests the coordination of one of the glycyl-NH groups and that involved in bonding should be assigned the low-frequency peak (see also figure 2). Two Amide I bands at 1702 and 1647 cm^{-1} are seen. In the ligand, corresponding maxima are observed at 1687 and 1656 cm^{-1} [13]. The new 1727 cm^{-1} peak in the complex proved the coordination to Au(III) of one O-atom of the COO^- group, resulting in a discrete C=O bond.

3.2. *Linear polarized IR spectra*

The NH- and C=O regions (figure 2) of the difference spectrum of the complex is characterized by a negative peak at 3277 cm^{-1} (ν_{NH}) and two oppositely oriented Amide I bands at 1647 and at 1702 cm^{-1}. The latter shows an opposed disposition of both peptide fragments (gly_1 and gly_2). The application of the reducing-difference procedure leads to the following results. The elimination of the 1647 cm^{-1} peak (figure 3) caused

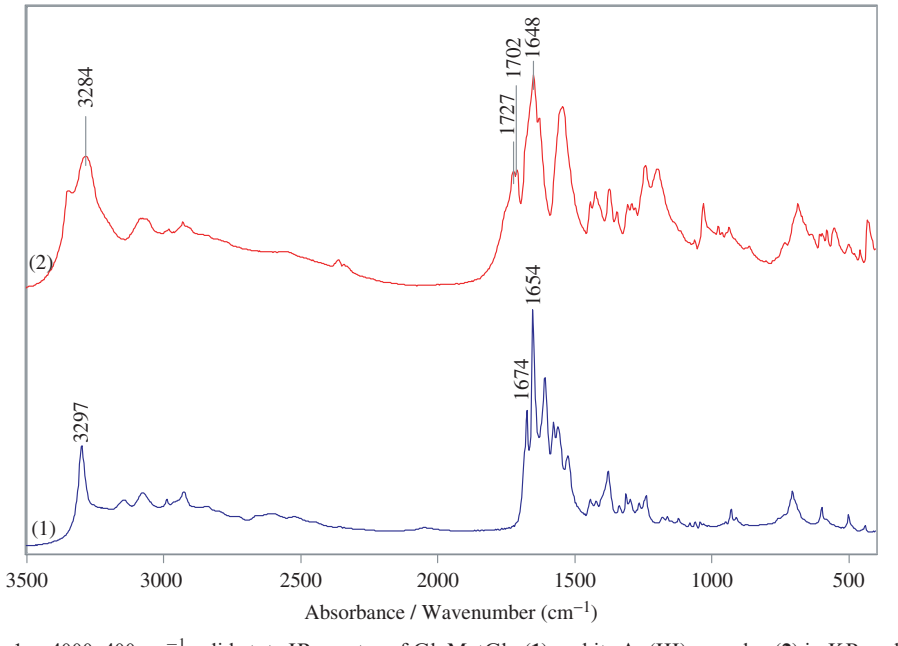


Figure 1. 4000–400 cm^{-1} solid state IR spectra of GlyMetGly (**1**) and its Au(III) complex (**2**) in KBr pellets.

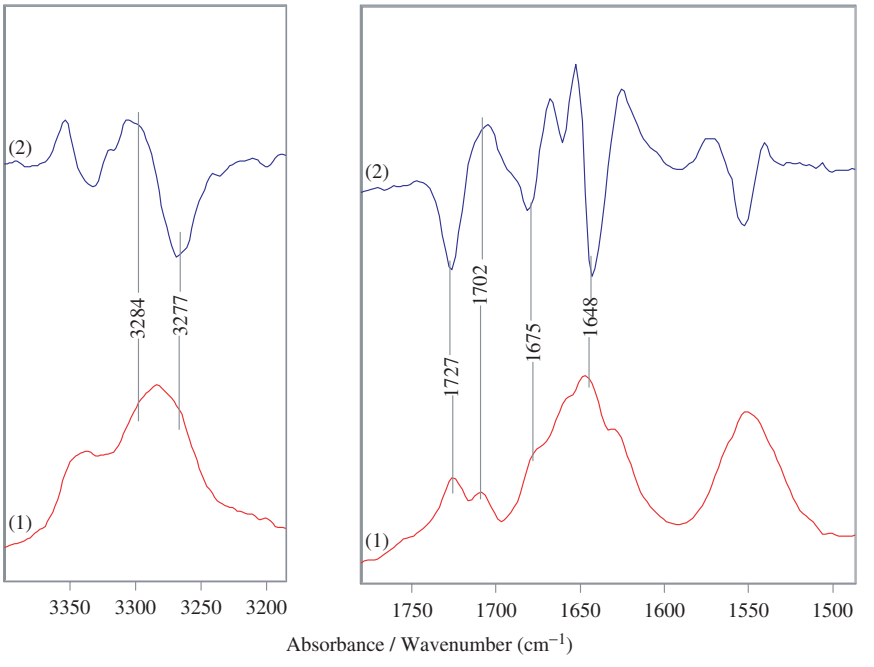


Figure 2. NH- and CO-stretching regions of non-polarized (1) and difference IR-LD spectra (2) of the Au(III)-GlyMetGly complex as a nematic liquid crystal suspension.

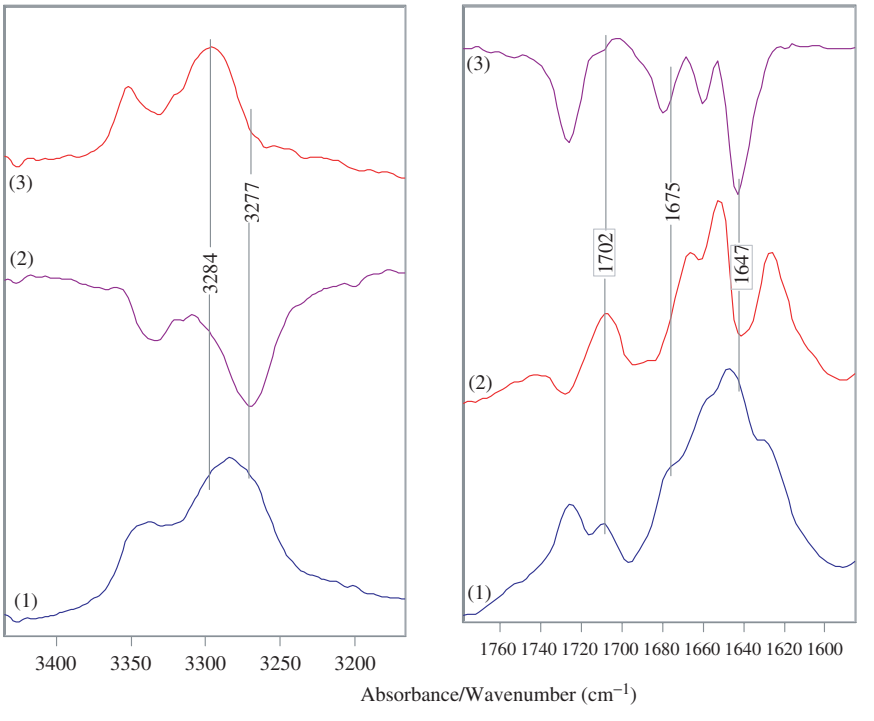


Figure 3. Non-polarized (1) and reduced IR-LD spectra of the Au(III)-GlyMetGly complex after elimination of the peaks at 1647 (2) and 1702 cm^{-1} (3).

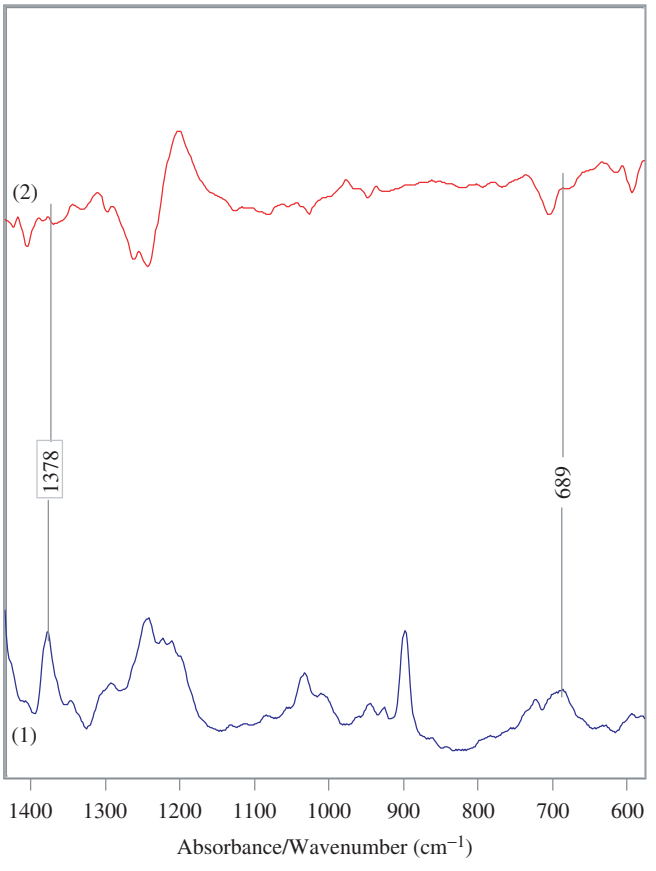
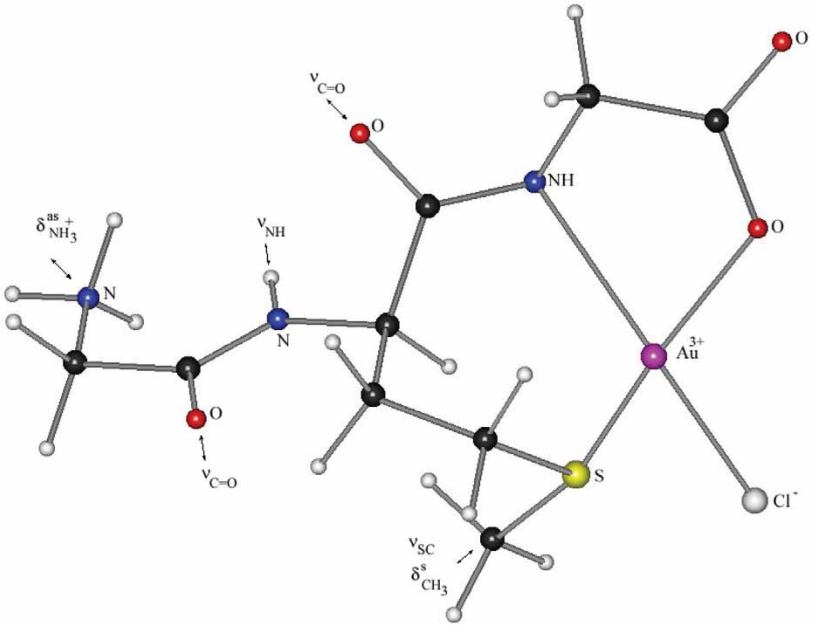


Figure 4. 1400–600 cm^{-1} non-polarized spectrum (1) and reduced IR-LD spectrum of the Au(III)-GlyMetGly complex (**2**) after elimination of the peak at 1378 cm^{-1}.

the disappearance of the high frequency NH maximum at 3284 cm^{-1}, indicating a co-linear disposition of their transition moments and, therefore, a *trans*-configuration of the non-coordinated amide fragment in the complex [14]. Elimination of 1702 cm^{-1} peak (figure 3) caused the second NH peak at 3277 cm^{-1} as well as the band at 1675 cm^{-1} ($\delta^{as}_{NH_3^+}$; 1673 cm^{-1} in the ligand; figure 1 [13]) to vanish. Moreover, elimination of the $\delta^{s}_{CH_3}$ bending mode at 1378 cm^{-1} (figure 4), causes the disappearance of ν_{CS} as a result of the co-linear transition moments of both fragments. The last procedure leads to the disappearance of the 689 cm^{-1} peak, thus assigning it to ν_{CS} of coordinated fragment. In the ligand the corresponding peak is at 703 cm^{-1} [13] (compare figures 1 and 2). These results lead to the stereochemistry of the complex cation shown in scheme 2.

3.3. *NMR data*

In similar methionine-containing di- and tripeptides, the (S)-CH_3 singlet in ^{1}H NMR should be observed in the 2.0 to 2.15 ppm range [5, 15, 16]. In the present case this peak



Scheme 2. Structure of the Au(III) complexes of tripeptide Gly-Met-Gly.

Table 1. ^{1}H and ^{13}C NMR δ chemical shifts (ppm) for GlyMetGly and its Au(III) complex.

	Gly-Met-Gly	Au^{3+}-Gly-Met-Gly
^{1}H		
$CH\text{-}_{met}$	4.72 (s)	4.94 (s)
$CH_2\text{-}_{met}$	1.85 (m)	1.90 (m)
$CH_2\text{-}_{met}$	2.50 (m)	2.47 (s)
$CH_3\text{-}_{met}$	1.95 (s)	2.28 (s)
$CH_2\text{-}_{gly1}$	3.71 (d)	3.79 (d)
$CH_2\text{-}_{gly2}$	3.60 (d)	3.95 (m)
^{13}C		
$CH\text{-}_{met}$	47.87	52.58
$CH_2\text{-}_{met}$	30.24	34.66
$CH_2\text{-}_{met}$	29.07	28.56
$CH_3\text{-}_{met}$	13.88	19.89
$CO\text{-}_{gly1}$	42.14	42.52
$CO\text{-}_{gly2}$	47.85	51.03
$CH_2\text{-}_{gly1}$	176.11	175.05
$COO\text{-}_{gly2}$	178.04	178.01
$COO\text{-}_{gly2}$	192.02	179.15

is observed at 1.95 ppm in the ligand and is shifted to 2.28 ppm in the complex (table 1). This is direct confirmation of coordination of the S-atom of the methionine fragment. The $CH_2\text{-}_{gly2}$ signals are also shifted in the complex (table 1), suggesting participation of the NH and COO^--groups of gly_2 fragment in coordination. This mode of coordination is confirmed by the ^{13}C NMR spectrum, showing shifted $CH_2\text{-}_{gly2}$ and (S)–CH_3 signals (table 1).

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