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Recommended Citation

IVANOVA, BOJIDARKA (2007) "Gold(III) Complex of Caffeine: Synthesis, Isolation and Spectroscopic Characterization," *Turkish Journal of Chemistry*: Vol. 31: No. 1, Article 12. Available at: https://journals.tubitak.gov.tr/chem/vol31/iss1/12

Gold(III) Complex of Caffeine: Synthesis, Isolation and Spectroscopic Characterization

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Au(III)-caffeine complex was synthesized and characterized by means of solid-state linear-dichroic infrared spectral analysis (IRLD), ^{1}H-NMR, MS, DSC and TGA methods. The caffeine (I) is monodentate and coordinated with metal ion through its N9 atom at molar ratio metal to ligand 1:1. The other 3 positions in the Au(III) coordination sphere are occupied by Cl$^-$, thus forming [Au^{3+}(C$_8$H$_{10}$N$_4$O$_2$)Cl$_3$] complex. IR-characteristic band assignment in the 4000-400 cm^{-1} IR region of pure ligand and corresponding Au(III)complex was performed.

Key Words: Caffeine, gold(III)-complex, IR-LD spectroscopy, ^{1}H-NMR.

Introduction

The metal complexes of purine and pyrimidine derivatives have been intensively studied because of their basic role in biochemical processes in the cell.[1,2] Binding of Ca(II) and Mg(II) cations to DNA and RNA as well as the Pt(II), Ru(II) and Au(III) metal ions, with a proposed antitumor effect, have been involved in some biological processes in vivo.[3−6] The study of the coordination ability of the last metals with purines and pyrimidines reveals in vitro the manner and mechanism of their coordination with DNA. Caffeine (3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione) could be used to examine the coordination ability on the N9 and O=(C6) positions as far as the N7 one is blocked by the –CH$_3$ group (Scheme 1).[3] For these reasons, the present paper deals with the synthesis, and spectral and structural characterization of a new Au(III)-caffeine complex, applying the methods of ^{1}H-NMR, MS and IRLD (IR spectral bands assignment and stereo-structural data) spectroscopies. The applicability of the last approach has been demonstrated already in a series of papers.[7−10]

(I)
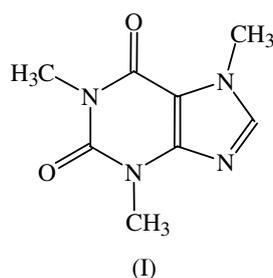
Experimental

Synthesis

The Au(III) complex with caffeine [Au(III) $(C_8H_{10}N_4O_2)Cl_3$] was prepared as follows: 10 mL of methanol solutions of 0.0977 g of $HAuCl_4.2H_2O$ (Merck) and 0.0987 g of caffeine(Bachem Organics) corresponding to a molar ratio of methanol to ligand 1:1 are mixed. After 20 days, a yellow precipitation is formed, filtered, washed with methanol and dried over P_2O_5 in air at 298 K. Yield: 22%. (Found: C, 19.26; H, 2.00; N, 11.32; Cl, 21.44%; Calc. for [Au(III) $(C_8H_{10}N_4O_2)Cl_3$]: C, 19.31; H, 2.03; N, 11, 26; Cl, 21.38%). The most intensive signal in the mass spectrum of the protonated salt is the peak at m/z 496.51, characteristic of the singly charged [Au(III) $(C_8H_{10}N_4O_2)Cl_3$] cation with molecule weight 496.52. These data indicated the formation of mononuclear Au(III)-complex with caffeine at a molar ratio of metal to ligand 1:1.

Methods

The IR spectra were measured on a Bomem-Michelson 100 FTIR-spectrometer (4000-400 cm^{-1}, 2 cm^{-1} resolution, 150 scans) equipped with a Perkin-Elmer wire-grid polarizer. The non-polarized solid-state IR spectra were recorded using the KBr disk technique. The oriented solid samples were obtained with a suspension in a nematic 4'-cyano-4'-alkylbicyclohexyl mixture (ZLI 1695, Merck), while its poor IR spectrum allows 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 about 2230 cm^{-1} additionally serves as an orientation indicator. The effective orientation of solid samples was achieved through the following procedure: 5 mg of the compound studied was mixed with the liquid crystal substance until a slightly viscous suspension was obtained. The prepared phase was placed between 2 KBr plates, which were rubbed out in advance in one direction. The grinding of the prepared mull in the rubbing direction promotes an additional orientation of the sample.[7−10]

The IRLD spectroscopy grounds and polarized IR-spectra interpretation for the difference-reduction procedure are shown in the literature.[12−15] The method consists of subtraction of a perpendicular spectrum, (IR$_s$), 90° angle rotation between the polarized light beam electric vector and the orientation of the sample from a parallel one (IR$_p$), obtained with a co-linear mutual orientation. The recorded difference (IR$_p$-IR$_s$) spectrum divided the parallel (A$_p$) and perpendicular (A$_s$) integrated absorbance of each band into positives, originating from transition moments that form average angles with the orientation direction (**n**) between 0° and 54.7°, and negative ones, corresponding to transition moments between 54.7° and 90°. After that, the perpendicular spectrum multiplied by the parameter *c* is subtracted from the parallel one and *c* has to vary until the elimination of a band or set of bands. The simultaneous disappearance of the bands in

the obtained (IR_p - $\boldsymbol{c}IR_s$) reduced IRLD spectrum indicates a co-linearity of the corresponding transition moments, thus giving rise to information regarding the mutual disposition of the molecular fragments. This elimination method is graphically carried out using a subtracting procedure attached to the program for the processing of IR spectra.

The ^{1}H-NMR measurements were obtained at 298 K with a Bruker DRX-400 spectrometer using 5 mm tubes and D_2O as solvent. The chemical shift reference was sodium 3-(trimethylsilyl)tetradeuteriopropionate.

The elemental analysis was performed by standard procedures for C, H (as CO_2, and H_2O), and N by Duma's method and Cl by titration with $Hg(NO_3)_2$ after wet digestion of the sample. The FAB mass spectra for the molecule weight determination were recorded on a Fisons VG Autospect instrument employing 3-nitrobenzyl alcohol as a matrix.

The thermogravimetric study was performed using Perkin-Elmer TGS2 apparatus. The calorimetric ones are performed on DSC-2C Perkin-Elmer equipment in argon.

Results and Discussion

IRLD spectral analysis of caffeine and its Au(III)-complex

The non-polarized IR-spectrum of caffeine (Figure 1.1) shows strong intensive peaks at 1698 and 1660 cm^{-1} assigned as $\nu_{C=O}$ and $\nu_{C=O} + \nu_{ring(imidazole)}$ modes.[15-17] The multiple characters could be explained by crystal field splitting. The 1598 and 1550 cm^{-1} peaks are assigned to $\nu_{ring(imidazole)} + \nu_{ring(primidine)}^{16-18}$ and the 1482 cm^{-1} one to $\nu_{C=N(imidazole)}$. The observed maxima at 761 and 748 cm^{-1} correspond to γ_{ring} (out of plane) + $\delta_{C=O}$ (in plane) and γ_{ring} modes.[16-18] The other relatively intensive maxima at 613 and 485 cm^{-1} should be assigned to γ_{ring} and $\gamma_{C=O}$, both out-of plane maxima. The application of the reducing-difference procedure for polarized IRLD spectra interpretation experimentally assigned and revealed the character of the corresponding peaks. The elimination of the relatively intensive ν_{CH} peak at 3115 cm^{-1} (Figure 1.2) does not provoke the vanishing of in-plane (i.p.) ring maxima (see below), similarly observed in other symmetric substituted heterocyclic derivatives,[19] thus indicating the deviation of the main i.p. (ring) mode axis (*II*).

The simultaneous disappearance of 1598, 1550 and 1482 cm^{-1} maxima (Figure 2.(a).2) confirmed their ν_{ring} assignment. The elimination of the 761 cm^{-1} peak (Figure 2.(b).2) lead with peaks at 748, 613 cm and 485 cm^{-1} proved their out-of-plane origin. The reduction of all of the multiple components in the 1700-1650 cm^{-1} region confirmed their origin as crystal field splitting bands.
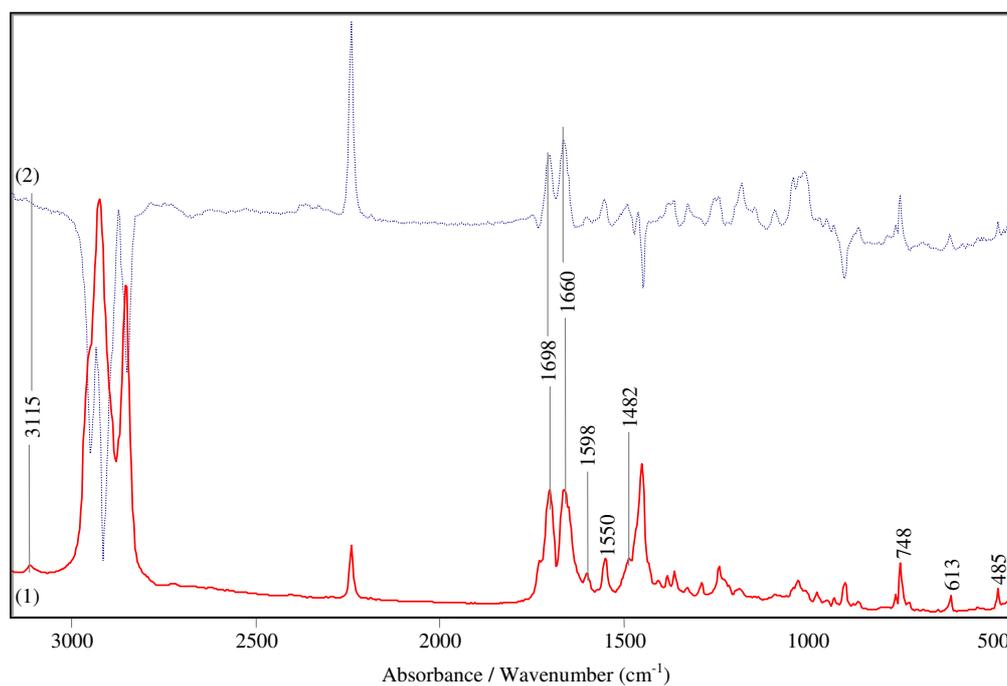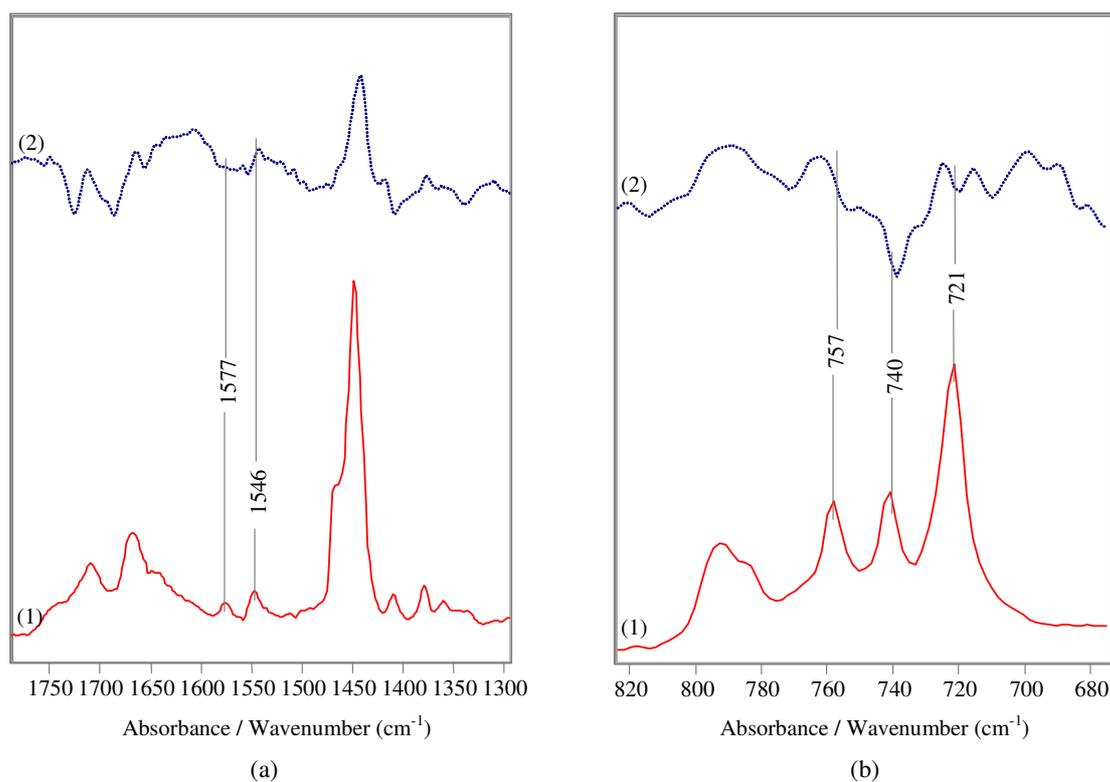
Figure 1. Non-polarized IR-(1) and reduced IR-LD (2) spectrum of caffeine after elimination of the 3115 cm^{-1} peak.
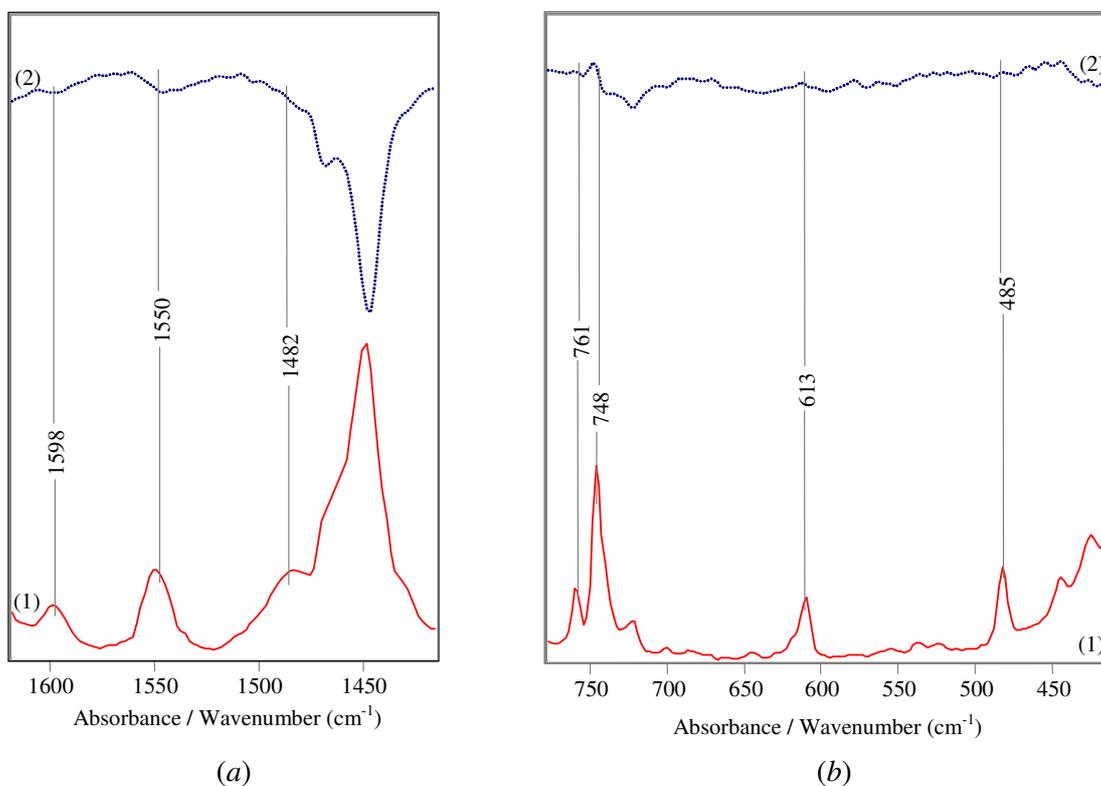

Figure 2. Non-polarized IR (1) and reduced IR-LD (2) spectra of caffeine after elimination of the peaks at (1) 1598 cm^{-1} and (2) 748 cm^{-1}.

The IR spectrum of the Au(III)-caffeine complex (Figure 3.1) is characterized by insignificant high frequency shifting of pairs of $\nu_{C=O}$ maxima to 1710 and 1666 cm^{-1} with a keeping of their multiple character. Similar behavior has been observed in Ca^{2+} and Mg^{2+} complexes with caffeine,[3] but the changes cannot correspond to the participation of O=C groups in coordination with Au^{3+} ion. In our case, the significant changes were connected with the ν ring in plane and $\gamma_{(ring)}$ peaks after complexation (compared to Figures 1.1 and 3.1). The 1598 and 1550 cm^{-1} maxima in the ligand (Figure 1.1) are low frequency shifted to 1577 and 1546 cm^{-1} in the complex (Figure 3.1). The low-intensive peak of $\nu_{C=N(imidazole)}$ in the ligand practically disappears in the complex. On the other hand, the 810-770 cm^{-1} region of the IR spectrum of the complex is characterized by a series of peaks at 791, 757, 740 and 721 cm^{-1}. These data assumed a monodentate coordination of caffeine through its N9 atom (*III*). A similar Zn^{2+}-complex has been obtained and crystallographically refined.[20] In addition, the peak at 3115 cm^{-1} practically disappears in the corresponding complex. The IRLD analysis yields the following results: (i) The elimination of the 1577 cm^{-1} peak (Figure 3.(*a*).2) with the 1546 cm^{-1} one, both i.p. modes; (ii) The disappearance of the 757, 791 and 721 cm^{-1} peaks (Figure 3.(*b*).2), all out-of-plane frequencies. (iii) Like in the IR spectrum of pure ligand the multiple character of the peak in the 1700-1600 cm^{-1} region confirmed their crystal field splitting origin.

Figure 3. Non-polarized IR (1) and reduced IR-LD (2) spectra of Au(III)-caffeine complex after elimination of the peaks at (1) 1577 cm^{-1} and (2) 757 cm^{-1}.

(II)   (III)
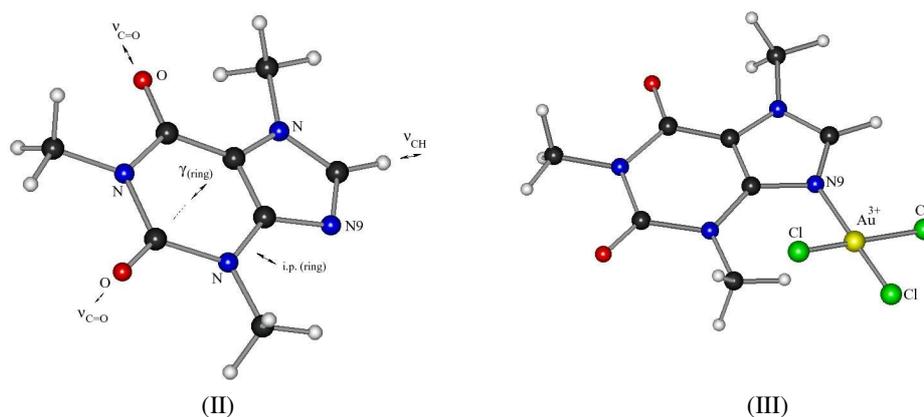
¹H-NMR data

The ¹H-NMR spectrum of caffeine in D_2O solution showed 4 relatively low intensive peaks at 3.30, 3.54, 3.90 and 7.76 ppm corresponding to the 3 CH_3-groups and CH, respectively.[21,22] The analogous spectrum of the Au(III)-caffeine complex is characterized by peaks at 3.28, 3.77, 3.98 and 7.66 ppm.

TGA and DSC data

The thermogravimetric and DSC data in the 300-500 K range indicated an absence of any solvent molecules included in the coordination spheres of obtained Au(III)-complex with caffeine.

Conclusion

The application of mass spectral and elemental analysis data indicated a quantitative amount of new complex as [Au(III) $(C_8H_{10}N_4O_2)Cl_3$] (*III*) with a metal to ligand molar ratio 1:1. Both spectroscopic ¹H-NMR and IRLD data indicated a monodentate coordination of caffeine though N9 with metal ion. In addition, 3 Cl— anions are coordinated through Au(III), thus forming a square planar geometry of $AuNCl_3$ chromophore.

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