# Spectral and Thermal Properties of Some Uranyl Complexes of Some Schiff-Bases Derived from Glycylglycine

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요  약.  우라늄 이온, $UO_2^{2+}$와 Schiff-base 와의 착화합물이 글리실글라이신과 살리실알데히드, 2-히드록시-1-나프트 알데히드, 2,3-디히드록시 벤즈알데히드, 그리고 2,4-디히드록시 벤즈알데히드와의 축합에 의해 합성되었으며 이들 착화합 물의 특성을 원소분석, 전도도 측정, 자기화율 측정, UV, IR, NMR 스펙트라와 DTA, TG, DSC 결과를 이용하여 조 사하였다. 구조와 열분해 메카니즘이 제안되었다.

**주제어:** 우라늄이온, 착화합물, 구조, 열분해

**ABSTRACT.** Complexes of uranyl ion $UO_2^{2+}$ with Schiff-bases obtained by condensing glycylglycine with salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2,3-dihydroxybenzaldehyde, and 2,4-dihydroxybenzaldehyde have been synthesized and characterized through elemental analysis, conductivity measurements, magnetic susceptibility determinations, u.v., i.r. and $^1H$ nmr spectra as well as d.t.a., t.g. and d.s.c. techniques. Structures and mechanisms of thermal decomposition are proposed.

**Keywords:** Glycylglycine Schiff-Bases, Uranyl Complexes, Structure and Thermal Properties, Decomposition Mechanism

## INTRODUCTION

Schiff-bases are important class of ligands in coordination chemistry and have pharmacological as well as physiological activities.[1-3] Metal complexes of Schiff-bases derived from amino-acids play an important roles as the basic compounds for modeling more complicated PLP-amino-acid Schiff-bases.[1-8] They are key intermediates in a variety of metabolic reactions involving amino-acids such as: decarboxylation, transamination, racemization and C-C bond cleavage, which are catalyzed by enzymes.[9,10] A number of studies have been undertaken on these and related systems in both solution and solid state with the aim of elucidating the reaction mechanisms.[11-20]

Interaction of Schiff-bases derived from salicylaldehyde and amino-acids with Mn(II) acetate and Cr(II) chloride in EtOH/H₂O medium gave complexes with composition Mn(sal-aa).2H₂O and Cr(sal-aa) Cl.2H₂O respectively (aa=Gly., Ala., and Phe.).[21] Iron(II) complexes of N-salicylidene- and N-(2-hydroxy-1-naphthalidene)-amino-acids (Gly., *l*-Ala., *l*-Phe., *l*-Val., *l*-Leu., *l*-His. and *l*-Trp.) have been

previously prepared and chracaterized.[22] Nolan and Soudi[23] have prepared and characterized Cu(II), Ni(II) and Co(II) complexes of the aspirine metabolite salicylglycine(HL) of stoichiometry $M(HL)_2$-solvate, but under basic conditions, Cu(II) forms the complex $Cu(LH_1)$. $2H_2O$. MeOH.

The complexation of uranyl ion $UO_2^{2+}$ and pervanadyl ion $VO_2^+$ with glycine have been investigated by spectrophotometric measurements in aqueous solution at 1M $NaClO_4$.[24] The spectra suggest that the coordination of the oxometal complexes is formed by the amino and carboxylate groups of glycine. Also, the preparation and reactivity of vanadium (IV) complex of N-salicylideneglycylglycine was described and it was characterized by elemental analysis, t.g.a., d.s.c., magnetic and spectroscopic techniques.[25]

It seems to be of interest to study the coordination behavior of the Schiff-bases of the biologically important glycylglycine towards uranyl ion, which is quite peculiar, both in its structural and coordination chemistry. However, we report the synthesis and characterization of a series of uranyl complexes with ligands derived from the reaction of glycylglycine with salicylaldehyde; 2-hydroxy-1-naphthaldehyde; 2,3-dihydroxybenzaldehyde; and 2,4-dihydroxybenzaldehyde. These complexes are characterized by elemental analyses; conductivity measurements; magnetic susceptibility determinations; u.v., i.r. and $^1H$ nmr spectra as well as d.t.a., t.g. and d.s.c. techniques.

## EXPERIMENTAL AND METHODS

### Materials

Salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2,3-dihydroxybenzaldehyde and 2,4-dihydroxybenzaldehyde were purchased from Fluka, uranyl acetate was purchased from Prolabo, and they were used as supplied. Other chemicals were reagent grade and were used without further purification.

### Preparation of the complexes

All complexes were prepared according to the following procedure. To a mixture of glycylglycine (10 mmol in 10 ml $H_2O$) and $Na_2CO_3$ (20 mmol),

the aldehyde (10 mmol in 10 ml EtOH) is added with stirring. The mixture was heated under reflux for two hours, after which the solution acquired a yellow color indicating the formation of the Schiff-base. The following ligands were obtained:



$L_1$ : R=H , $L_3$ : R=3-OH , $L_4$ : R=4-OH



$L_2$
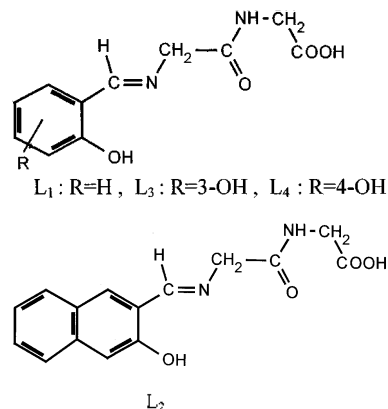
Uranyl acetate (10 mmol) was dissolved in 20 ml EtOH and added to the Schiff-base ligand with stirring. Salicylaldehyde Schiff-base complex was precipitated immediately, while the complexes of the other Schiff-bases were precipitated after stirring for one hour. The complexes were filtered, washed with $H_2O$ and EtOH and dried under vacuum.

### Apparatus

Microanalyses were performed on an Alco CHNS-932 analyzer. Uranium concentration was determined on a Fison ICP emission spectrophotometer at wavelengths 367.007, 385.958 and 409.014 nm using uranium standard solution. Conductivity measurements were carried out at 25 °C on freshly prepared $10^{-3}$M DMSO solutions of the complexes using WTW conductivity meter fitted with Orion conductivity cell. I.r. spectra were recorded on Nicolet Impact 400 and Perkin-Elmer 598 spectrophotometers using nujol mull and KBr techniques. U.v. spectra were obtained using Beckman Du-640 spectrophotometer for freshly prepared $10^{-5}$M DMSO solutions. $^1H$ nmr spectra were obtained with Bruker AMX-300 in DMSO-$d_6$ using TMS as internal standard. D.t.a., t.g. and d.s.c. were measured on a Shimadzu XD-30 thermal analyzer with heating rate 10 °C/min. under atmospheric oxygen. X-ray powder diffraction was performed using a Shi-

*Table* 1. Analytical and physical data for the uranyl complexes

| Complex | Colour | Mol. Wt. | C%o | | H%o | | N%o | | U%o | | $\Lambda_M^*$ DMSO | $\lambda_{nm}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | | |
| [UO$_2$L$_1$].H$_2$O | Orange | 521.77 | 25.1 | 25.3 | 2.4 | 2.1 | 4.2 | 4.4 | 46.1 | 45.6 | 3.96 | 276, 330 |
| [UO$_2$L$_2$].H$_2$O | light brown | 573.25 | 31.5 | 31.4 | 2.4 | 2.4 | 4.9 | 4.7 | 40.4 | 40.5 | 4.01 | 303, 365 |
| [UO$_2$L$_3$].H$_2$O | light brown | 538.77 | 24.5 | 24.5 | 2.0 | 2.1 | 5.1 | 5.0 | 44.4 | 44.2 | 3.91 | 285, 335 |
| [UO$_2$L$_4$].4H$_2$O | Light orange | 592.77 | 22.3 | 22.3 | 2.8 | 2.7 | 4.7 | 4.7 | 42.5 | 41.9 | 2.68 | 288, 340 |

*$\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$

madzu XD-3 diffractometer with Cu-K$_\alpha$ radiation. Magnetic susceptibilities of the complexes were measured using modified Gouy method on Johnson Matthey magnetic balance.

## RESULTS AND DISCUSSION

Results of elemental analyses are shown in *Table* 1 and indicate that the complexes under study have 1:1 stoichiometry. All complexes are dark colored solids insoluble in alcohol, acetone, pyridine, diethylether, ethylene chloride and partially soluble in DMF and DMSO. The molar conductances of 10$^{-3}$M DMSO solutions of the uranyl complexes are too low to account for any dissociation of the complexes. All complexes are diamagnetic as expected for an UO$_2^{2+}$ ion.

### $^1$H NMR spectra

Room temperature $^1$H nmr spectra (DMSO-d$_6$) show three groups of signals at $\delta$=6.6-7.7 ppm, five groups of signals at $\delta$=7.2-8.4 ppm, two groups of signals at $\delta$=6.4-7.2 ppm and three groups of signals at $\delta$=6.1-7.5 ppm for the aromatic protons of the uranyl complexes of L$_1$, L$_2$, L$_3$, and L$_4$ respectively. The two -CH$_2$- groups of the glycylglycine moiety appear at $\delta$=5.51(s) and $\delta$=5.06(d) ppm, $\delta$=5.7(s) and $\delta$=5.07(d) ppm, $\delta$=5.57(s) and $\delta$=5.08(d) ppm, $\delta$=5.45 (s) and $\delta$=5.0 (d) for the above mentioned complexes respectively. The characteristic signals of the azomethine group (>C=N) are observed at $\delta$=9.35, 10.2, 9.37 and 9.25 ppm for the complexes respectively.[2b] On the other hand, the o-OH protons on the phenyl and naphthyl rings did not observed.[2b] This confirms that bonding to the ligands takes place through displacement of the protons from the o-OH groups on the phenyl and naphthyl rings. The m-OH and p-OH protons of ligands L$_3$ and L$_4$ resonate at $\delta$=8.15 and $\delta$=10 ppm indicating that they do not take place in bonding to the uranyl ion. The -NH protons appeared at $\delta$=10.2, 10.43, 10.36 and 10.28 ppm respectively. Therefore, the NH groups are not involved in bonding through complex formation. The protons of o-OH, p-OH and NH groups on the ligands are exchangeable with D$_2$O of all complexes. The disappearance of the COOH signal in the complex spectra indicates the ionization of the carboxylic group.

### I.R. spectra

The IR spectra of the complexes are quite complex (*Table* 2), however, a few assignments are helpful to the structural work. Water is detected by a broad band due to its -OH centered at 3580, 3556, 3600 and 3500 cm$^{-1}$ respectively. The Strong sharp absorption bands of the amide ($\nu_{NH}$) appeared at 3370, 3344, 3320 and 3287 cm$^{-1}$. Sharp bands at 3105, 3099, 2945 and 2928 cm$^{-1}$ in the spectra of the complexes may be assigned to $\nu_{as}$(CH$_2$) (*Table* 2).

Strong broad split bands, in the C=O stretching region, are observed in the spectra of all complexes. They have maxima at: 1658, 1639 and 1595 cm$^{-1}$ for [UO$_2$L$_1$].H$_2$O: 1660, 1640, 1605 and 1578 cm$^{-1}$ for [UO$_2$L$_2$].H$_2$O: 1653, 1629, 1596 and 1556 cm$^{-1}$ for [UO$_2$L$_3$].H$_2$O; and 1631, 1599 and 1560 cm$^{-1}$ for [UO$_2$L$_4$].4H$_2$O. These bands may be assigned to: $\nu$(CH=N) indicative of imine structure, the CONH group (amide I band)[27] and the coordinate carboxylate group.[28] The $\nu_{sym}$(COO$^-$) bands are observed at 1422, 1430, 1407 and 1390 cm$^{-1}$ respectively.[29,30]

The strongest evidence for complexation of the uranyl ion with the Schiff-bases under investiga-

*Table* 2. Infrared spectral bands of the uranyl complexes

| Complex<br>Assignment | $[UO_2L_1].H_2O$ | $[UO_2L_2].H_2O$ | $[UO_2L_3].H_2O$ | $[UO_2L_4].4H_2O$ |
|---|---|---|---|---|
| $v(H_2O)$ | 3580 sh. | 3556 sh. | 3600 sh. | 3500 sh. |
| $v(NH)$ | 3370 sh. | 3344 br. | 3320 sh. | 3287 sh. |
| $v_{as}(CH_2)$ | 3105 sh. | 3099 br.<br>3936 w. | 2945 w. | 2928 s.br. |
| $v(CH-N)$ | 1658⎤ | 1660⎤ | 1653⎤ | 1631⎤ |
| $v(-CONH)$ | 1639⎬ s.br. | 1640⎬ s.br. | 1629⎬ s.br. | 1599⎬ s.br. |
| $v_{as}(COO^-)$ | 1595⎦ | 1605�<br>1578⎦ | 1596�<br>1556⎦ | 1560⎦ |
| $v_{sym}(COO^-)$ | 1422 sh. | 1430 sh. | 1407 sh. | 1390 sh. |
| $v_{as}(O-U-O)$ | 914 v.s. | 910 v.s. | 918 v.s. | 910 v.s. |

tion is the appearance of characteristic stretching frequency of dioxouranium ion $UO_2^{2-}$ in the i.r. spectra of the formed complexes. Accordingly, strong bands in the region 910-918 cm$^{-1}$ (*Table* 2) in the spectra of the studied complexes are assigned to the asymmetric stretching frequency $v_{as}(O=U=O)$.[31,32]

### U.V. spectra

The electronic spectra of the complexes in $10^{-5}M$ DMSO solutions (*Table* 1) show a number of bands in the u.v. region. The absorption bands appearing at 276 nm (L$_1$), 303 nm (L$_2$), 285 nm (L$_3$) and 288 nm (L$_4$) may be attributed to benzenoid $\Pi \rightarrow \Pi^*$ transitions. Absorption bands at 330 nm (L$_1$), 365 nm (L$_2$), 335 nm (L$_3$) and 340 nm (L$_4$) are assigned to conjugate imine $\Pi \rightarrow \Pi^*$ transitions of the aldimine which were observed with other Schiff-bases.[33]

### Thermal studies

The results of simultaneous d.t.a.-t.g. and d.s.c. analyses of the complexes are shown in *Fig.* 1 and *Table* 3. The abrupt weight loss observed in both t.g. and d.t.a. curves at temperatures 87 °C, 50-170 °C, 72-130 °C. 50-130 °C and the corresponding endothermic peaks are due to dehydration.[34] This is responsible for the color change from light brown to brown ($[UO_2L_2].H_2O$ and $[UO_2L_3].H_2O$), and from orange to brown ($[UO_2L_1].H_2O$ and $[UO_2L_4].4H_2O$). Since, the dehydration temperature of the complexes $[UO_2L_3].H_2O$ and $[UO_2L_4].4H_2O$ is almost the same (72-130 °C), this may be due to both complexes have the same substituents in benzene ring (two -OH groups). The i.r. spectra of the complexes and their dehydrated forms show no differ-
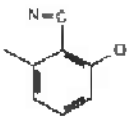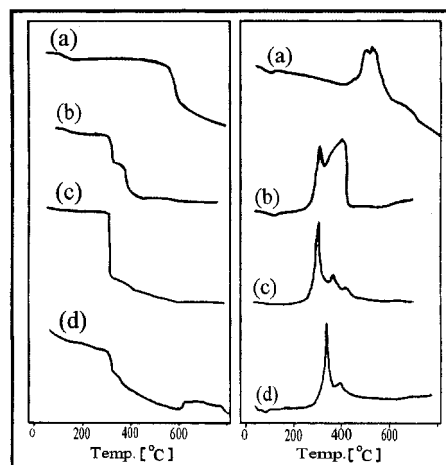


*Fig.* 1. D.t.a. and t.g.a. spectra of the complexes. (a) $[UO_2L_1].H_2O.$ (b) $[UO_2L_2].H_2O.$ (c) $[UO_2L_3].H_2O.$ (d) $[UO_2L_4].4H_2O.$

ences. This indicate that this part of hydration water makes no contribution to the lattice forces and is trapped in the crystal voids.[35,36]

Moreover, the X-ray pattern of the complexes $[UO_2L_3].H_2O$ and $[UO_2L_4].4H_2O$ after dehydration is characterized by a number of reflections compared to before dehydration (*Fig.* 2). This indicates that degree of crystallinity is obtained after dehydration.[37]

The exothermic peaks within the temperature range 340-373 °C for $[UO_2L_3].H_2O$ and 350 °C for $[UO_2L_1].H_2O$ are assigned to thermal degradation and partial decomposition as indicated from their thermoproducts in the same temperature range. The sharp exothermic peaks in the temperature range

*Table* 3. D.t.a., t.g.a. and d.s.c. peaks and their assignments

| Complex | D.t.a. and d.s.c. Exo. | Endo. | Assignment | T.g. Found(Calcd.) (%) | Loss type |
|---|---|---|---|---|---|
| [UO₂L₁].H₂O | 87(DTA) | - | Dehydration process | 3.2 (3.14) | H₂O |
| | - | 340(DSC) | Degradation | - | - |
| | - | 373(DTA) | Partial decomposition | - | - |
| | 420(DSC) | - | Fusion and vaporization | - | - |
| | - | 433(DSC) | Final degradation and decomposition | 17.46 (17.89) | --NHCH₂COOH |
| | 490(DTA) | - | Solid state mechanism | - | - |
| [UO₂L₂].H₂O | 50-170(DSC) | - | Dehydration process | 3.14 (3.13) | H₂O |
| | - | 350(DTA) | Partial decomposition | 21.48 (20.8) | --CH₂CONHCH₂ |
| | 380(DSC) | - | Fusion and vaporization | 26.4 (25.7) | (structure) |
| | - | 465(DTA) | Final decomposition | - | - |
| | - | 500(DSC) | Solid state reaction | - | - |
| [UO₂L₃].H₂O | 72-130(DSC) | - | Dehydration | 3.3 (3.5) | H₂O |
| | - | 341(DTA) | Partial decomposition | - | - |
| | 395(DSC) | - | Fusion and vaporization | - | Side chain and ligand |
| | - | 409(DTA) | Final decomposition | 48.19 (47.49) | - |
| | - | 473(DTA) | Solid state reaction | - | - |
| [UO₂L₄].4H₂O | 50-70(DSC) 70-130(DSC) | - | Dehydration process takes place in two steps | 12.14 (12.14) | 4 H₂O |
| | - | 300-335(DTA) | Partial decomposition | 12.48 (12.14) | --NHCH₂COOH |
| | 389(DSC) | - | Fusion and vaporization | - | - |
| | - | 398(DTA) | Oxidation degradation | - | - |
| | - | 420(DTA) | Final decomposition | - | - |

Complexes [UO₂L₂].H₂O and [UO₂L₃].H₂O have stability zones at 600-800 °C which are attributed to the formation of metal oxides.
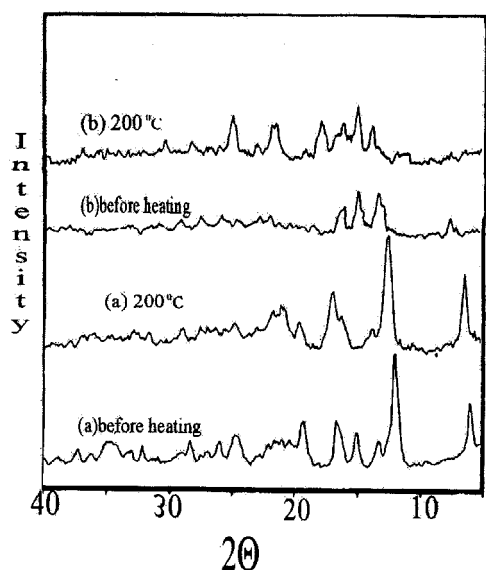


*Fig.* 2. X-ray diffraction pattern of the complexes. [UO₂L₂].H₂O (b) [UO₂L₄].4H₂O.

(380-395 °C) for the complexes [UO₂L₂].H₂O. [UO₂L₃].H₂O and [UO₂L₄].4H₂O are attributed to fusion and vaporization,[34] followed by an exothermic peaks at the temperature range (409-465 °C) corresponding to the final decomposition.[35]

T.g. curves (*Fig.* 1) indicate that decomposition of the anhydrous complexes follow immediately after dehydration process with different mechanisms.[35] The partial decomposition of all complexes start at temperatures 373 °C, 350 °C, 341 °C and 300 °C. As demonstrated by t.g. and i.r. spectra, neither amide carbonyl at 1640 cm⁻¹ nor N-H in the range 3320-3370 cm⁻¹ are present. This implies the mechanism of decomposition of the complexes [UO₂L₂].H₂O and [UO₂L₄].4H₂O. which does begin by scission of the side chain of the ligand --CH—C-NH-CH₂-COOH.
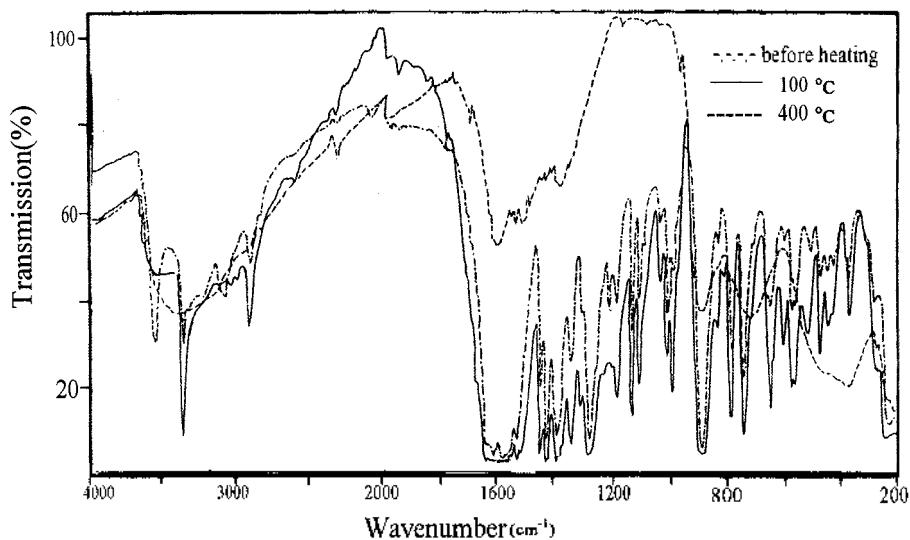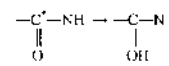
But for the complex [UO₂L₁].H₂O, the pathway of ther

*Fig.* 3. Infrared spectra of the $[UO_2L_1].H_2O$ complex before and after heating.

mal decomposition can be represented as follows: complex $[UO_2 L_1].H_2O - 100\ °C\rightarrow$ anhydrous form and its i.r. spectrum of the anhydrous form (*Fig.* 3) shows the absence of –CONH– at 1640 cm[1,38] This means that the transformation

$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH \rightarrow -\overset{\overset{\displaystyle OH}{|}}{C}-N$$

takes place since –C–O bands at 1200 and 1300 cm^{-1} are still present[39] with increasing intensity after dehydration, then decomposition start by fission of the –C–/–N–CH$_2$–COOH. The products of thermal decomposition of the complexes are seen in *Table* 3.

Based on the above analytical data and physicochemical properties, the following structure is proposed in which uranyl ion is coordinated through azomethine nitrogen, oxygen of the ionized phenolic hydroxyl group, the carbonyl and caboxylate groups of the glycine moeity.
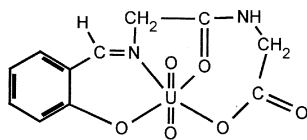


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