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Spectroscopic Studies and Thermal Analysis of Some New Metal Complexes with Levofloxacin and Glycine

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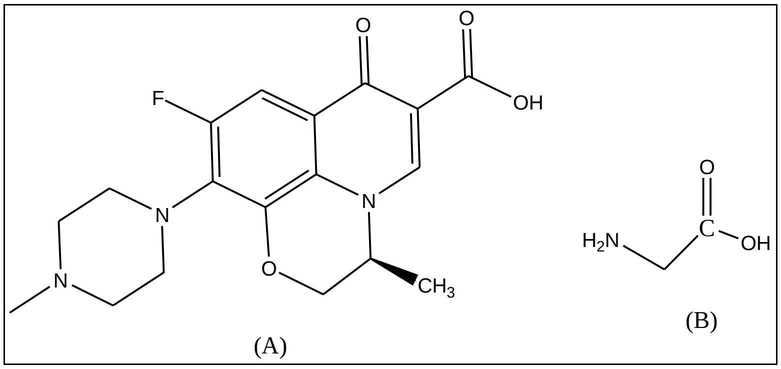
ABSTRACT

In this study, mixed ligand complexes derived from levofloxacin as primary ligand and glycine as secondary ligand have been prepared and characterized by conventional techniques including elemental analyses, infrared, electronic spectra, ^{1}H NMR, thermal analyses and XRD. The infrared spectral data show that the chelation behavior of the ligands toward transition metal ions is through pyridone, carboxylic group of levofloxacin and nitrogen atom of amine group and one oxygen atom of carboxylic of glycine. Thermal analyses show that the complexes lose water molecules of hydration initially and subsequently expel anionic part and organic ligands in continuous steps leaving metal or metal oxide as a final product.

Keywords: Fluoroquinolone; Glycine; Spectroscopic; Thermal; XRD

INTRODUCTION

Levofloxacin (levo) (Scheme 1A) is one of the third generation fluoroquinolones drug class that exhibits potent activity against Gram-positive and Gram-negative bacteria [1,2] with a wide variety of brand trade names such as Levaquin (US) and Tavanic (EU). Levofloxacin is the pure (-)-(*S*)-enantiomer of the racemic ofloxacin which possesses a methyl group at the C-3 position with an (S)-configuration of the oxazine ring [3].



Scheme 1: (A)(S)-9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-3,7-dihydro-2H-[1,4]oxazino[2,3,4-j]quinoline-6-carboxylic acid, (B) glycine (Gly)

Today, little articles have been reported on the coordination properties of levofloxacin with the zinc metal ion. Paula C Huber et al. refer a single zinc complex of levofloxacin and its antimicrobial properties [4] whereas Tarushi et al. presents a full study of an also single zinc complex with levofloxacin with distorted octahedral geometry and its biological properties [5].

Glycine (abbreviated as Gly or G) (Scheme 1B) is the amino acid that has a single hydrogen atom as its side chain. It is the simplest possible amino acid. The chemical formula of glycine is NH2-CH2-COOH. In this evolving context, synthesis of mixed ligand metal complexes of Levo as primary ligand and Gly as secondary ligand and their characterization by various physical and spectral methods such as melting point, molar conductivities, magnetic properties, elemental analysis, infrared, 1H NMR, UV-vis. and XRD spectroscopy as well as thermo gravimetric have been taken up.

MATERIALS AND METHODS

Chemicals

All chemicals used for the preparation of the complexes were of analytical reagent grade, commercially available from different sources and used without further purification. Levofloxacin used in this study was purchased from Obour Pharmaceutical Industrial Company. Glycine, ethanol, $FeCl_3.6H_2O$, $AgNO_3$, and K_2CrO_4 were purchased from Fluka Chemical Co. $Zn(CH_3COO)_2.2H_2O$, $ZrOCl_2.8H_2O$, $LaCl_3.7H_2O$, $ThCl_4$ and $UO_2(CH_3COO)_2.2H_2O$ from Aldrich Chemical Co.

Synthesis of Mixed Ligand Metal Complexes

The biege solid mixed complex $[Zn(Levo)(Gly)(H_2O)_2].10H_2O$ was prepared by mixing 1 mmol (0.361 g) of hot saturated ethanolic solution of the first ligand (Levo) with 2 mmol (0.112 g) KOH and 1 mmol (0.075 g) of Gly with the same ratio 1mmol (0.2195 g) of zinc(II) acetate dihydrate. The mixture was refluxed for 6 h. The biege precipitate was filtered off, washed several times with ethanol until the filtrate becomes clear and dried under vacuum over anhydrous $CaCl_2$.

The yellow, pale yellow, yellow and dark yellow solid complexes of $[ZrO(Levo)(Gly)(H_2O)].3H_2O$, $[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$, $[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$ and $[UO_2(Levo)(Gly)].H_2O$ were prepared in a similar manner described above by using ethanol as a solvent and $ZrOCl_2.8H_2O$, $LaCl_3.7H_2O$, $ThCl_4$ and $UO_2(CH_3COO)_2.2H_2O$, respectively, in 1:1:1:2 (Levo:metal:Gly:KOH) molar ratio. Single crystal suitable for X-ray crystallographic measurements was not obtained.

Instruments

Elemental C, H and N analysis was carried out on a Perkin Elmer CHN 2400. The percentage of the metal ions were determined gravimetrically by transforming the solid products into metal or metal oxide and also determined by using atomic absorption method. Spectrometer model PYE-UNICAM SP 1900 fitted with the corresponding lamp was used for this purposed. IR spectra were recorded on FTIR 460 PLUS (KBr discs) in the range from 4000-400 cm^{-1}, ^1H NMR spectra were recorded on Varian Mercury VX-300 NMR Spectrometer using DMSO-d_6 as solvent. Electronic spectra were obtained using UV-3101PC Shimadzu. The absorption spectra were recorded as solutions in DMSO. TGA-DTG measurements were run under N_2 atmosphere within the temperature range from room temperature to 1000°C using TGA-50H Shimadzu, the mass of sample was accurately weighted out in an aluminum crucible. XRD analyses were carried out by using a Philips Analytical X-ray BV, diffractometer type PW 1840. Radiation was provided by a copper target (Cu anode 2,000 W) high intensity X-ray tube operated at 40 kV and 25 mA. Magnetic measurements were done on a Sherwood scientific magnetic balance using Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Molar conductivities of the solution of the ligand and metal complexes in DMF at 1×10^{-3} M were measured on CONSORT K410. All measurements were carried out at ambient temperature with freshly prepared solutions.

RESULTS AND DISCUSSION

The complexes of levofloxacin (Levo) with Zn(II), Zr(IV), La(III), Th(IV) and U(VI) in the presence of glycine were synthesized and characterized. The formulas pattern and the geometry of the complexes were assigned on the basis of physico-chemical parameters such as conductance measurements, magnetic susceptibilities and spectral measurements. The molar conductance values of levofloxacin, glycine and their metal complexes in DMSO with standard reference, using 1×10^{-3} M solutions at room temperature, were done. The molar conductance values for La(III) found at 85.5 showed 1:1 electrolyte, while Th(IV) with a value 195.4 S cm^2 mol^{-1} showed 1:2 electrolyte (Table 1) [6]. The data obtained from molar conductivity measurements and qualitative reactions showed that La(III) and Th(IV) complexes are electrolytes with chloride as counter ions (outside the complex sphere). The magnetic susceptibility measurments for Zn(II) d^0, Zr(IV) d^0, La(III) d^0, Th(IV) d^0 and U(VI) d^0 complexes indicated that the complexes were found as diamagnetism.

Table 1: Elemental analysis and physico-analytical data for levofloxacin (Levo), glycine (Gly) and their metal complexes

Compounds M.Wt. (M.F.)	Yield%	Mp/°C	Color	Found (Calcd.) (%)					Λ
				C	H	N	M	Cl	S cm^2 mol^{-1}
Levo	-	223	White yellow	59.75	5.5	11.59	-	-	17
361.4 ($C_{18}H_{20}FN_3O_4$)				-59.77	-5.53	-11.62			
Gly	-	232	White	31.94	6.62	18.61	-	-	44.2
75.07 ($C_2H_5NO_2$)				-31.97	-6.66	-18.65			
[Zn(Levo)(Gly)(H_2O)$_2$].10H_2O	78.88	270	Biege	33.51	6.53	7.8	9.1		7
715.41 ($ZnC_{20}H_{47}FN_4O_{18}$)				-33.55	-6.57	-7.83	-9.14	-	
[ZrO(Levo)(Gly)(H_2O)].3H_2O	80.19	277	Yellow	39.1	5.02	9.1	14.82		10
613.22 ($ZrC_{20}H_{31}FN_4O_{11}$)				-39.14	-5.06	-9.13	-14.88	-	
[La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O	82.2	170	Pale yellow	35.22	4.53	8.19	20.39	5.19	85.5
680.41 ($LaC_{20}H_{31}FN_4O_{10}Cl$)				-35.27	-4.56	-8.23	-20.42	-5.22	
[Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O	90.42	283	Yellow	29.65	3.8	6.9	28.65	8.75	195.4
809.04 ($ThC_{20}H_{31}FN_4O_{10}Cl_2$)				-29.66	-3.83	-6.92	-28.68	-8.78	
[UO_2(Levo)(Gly)].H_2O	85.71	295	Dark yellow	33.2	3.44	7.73	32.95		9.5
722.03 ($UC_{20}H_{25}FN_4O_9$)				-33.24	-3.46	-7.76	-32.97	-	

IR Absorption Spectra

The mid infrared spectra of Levo, Gly and their metal complexes were discussed in this section (Figure 1). Levo is expected to act as a bidentate ligand, with possible coordination sites being the pyridone oxygen and carboxylic group. Study and comparison of the IR spectra of levo and the metal complexes imply that levo is bidentate in nature, with the pyridone oxygen and one oxygen of carboxylic group as the two coordination sites. Also, Gly reacted with metal ions a bidentate ligand through nitrogen atom of amine group and one oxygen atom of carboxylic group. In the infrared spectrum of Levo, the two bands at 1724 and 1620 cm^{-1} (Table 2), were assigned to the $\nu(C{=}O)_{carboxyl}$ and $\nu(C{=}O)_{pyridone}$ vibration frequencies [7,8]. The free amino acids exhibit $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ around 3420 and 3169 cm^{-1}, respectively. Very strong band observed at 1604 cm^{-1} in the free Gly ligand is assigned to the carbonyl stretching vibration and The binding vibration of NH_2 found at 1604 cm^{-1} [9-11]. In the spectra of the complexes, the band corresponding to the carboxylic group appears with $\Delta\nu > 200$ cm^{-1}, indicating a monodentate coordination mode of the carboxylato group of the ligands [12-16]. The characteristic band for the pyridone stretch $\nu(C{=}O)$ found at 1620 cm^{-1}, this band is shifted to the lower values of 1593 cm^{-1} for Zn(II), 1540 cm^{-1} for Zr(IV), 1577 cm^{-1} for La(III), 1587 cm^{-1} for Th(IV), 1564 cm^{-1} for U(VI) upon coordination [17].

The coordination of the metal ions via oxygen and nitrogen atoms is confirmed by the ν(M-O) and ν(M-N) bands at 662w, 622vw, 507w cm^{-1} for Zn(II), 687vw, 642vw, 553vw, 501m cm^{-1} for Zr(IV), 687w, 505w cm^{-1} for La(III), 684w, 595vw, 543vw, 501m cm^{-1} for Th(IV) and 679m, 615vw, 547vw, 505w cm^{-1} for U(VI). Also, the data indicated that $\nu(Zr{=}O)$ are found as medium band at 812 cm^{-1}, respectively [18,19].

Proposed structures for the complexes are shown in Scheme 2. The data showed that the $\nu_{as}(U{=}O)$ occurs at 919 cm^{-1} as a strong singlet and $\nu_s(U{=}O)$ is observed at 813 cm^{-1}. These assignments for the uranyl agree with those for many dioxouranium(VI) complexes [20,21]. The $\nu_s(U{=}O)$ value was used according to the known method [22,23], to calculate both the U=O bond stretching force constant, F(U=O), and bond length. The calculated values are 1.747 Å and 641.04 Nm^{-1}.

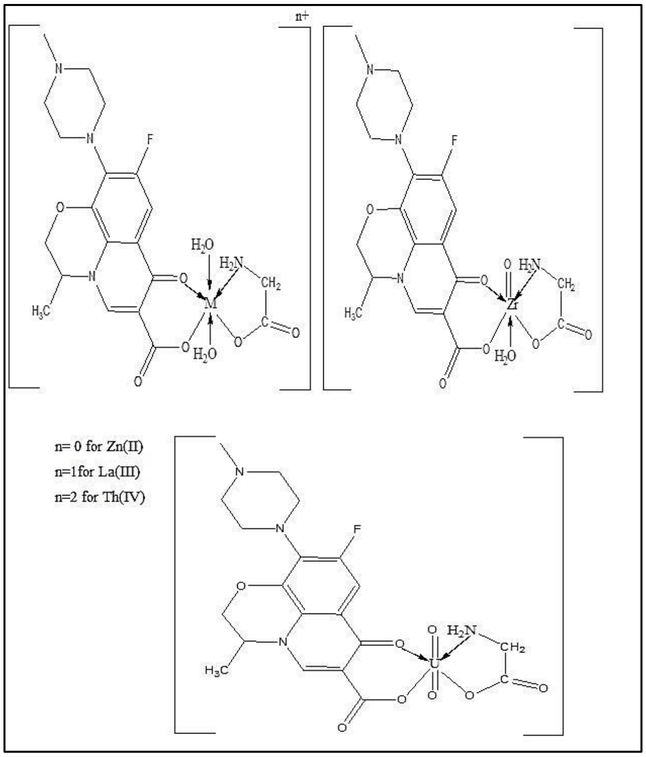
$$\acute{\upsilon} = \frac{1}{2}\pi c\sqrt{F/\mathrm{M_O}}$$

$\mathrm{M_O}$=mass of oxygen

$$\mathrm{r(U=O)} = \frac{1.08}{\sqrt[3]{\mathrm{F}}} + 1.17$$

Or

$$\mathrm{r(U=O)} = 1.993\ \mathrm{F}^{-1/3} + 0.66$$



Scheme 2: The coordination mode of Zn(II), Zr(IV), La(III), Th(IV) and U(VI) with mixed ligand

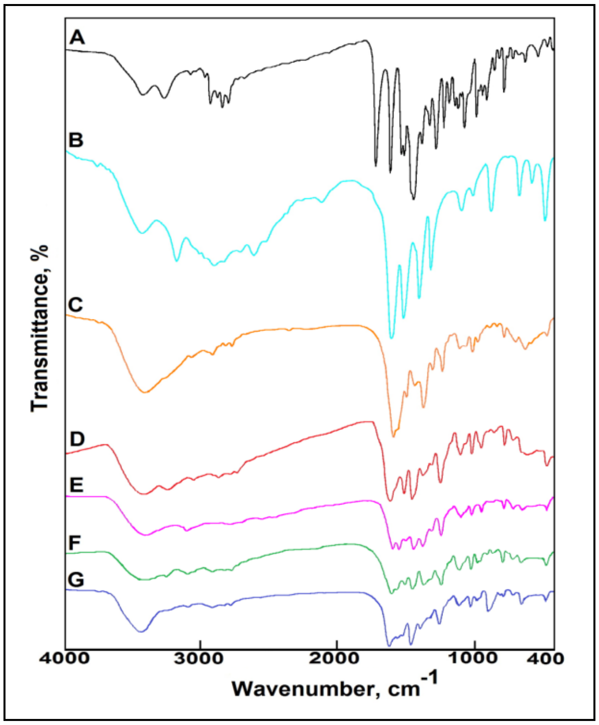


Figure 1: Infrared spectra for (A) Levo, (B) Gly, (C) [Zn(Levo)(Gly)(H_2O)$_2$].10H_2O, (D) [ZrO(Levo)(Gly)(H_2O)].3H_2O, (E) [La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O, (F) [Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O and (G) [UO_2(Levo)(Gly)].H_2O

Table 2: IR wavenumbers (cm^{-1}) and tentative assignments of the most important bands in free ligands and mixed complexes

Compounds	ν(O-H); H_2O; COOH,	ν(NH_2)	ν(C=O); COOH	$ν_{as}(COO^-)$	ν(C=O)	$ν_s(COO^-)$	$ν_{as}$(U=O) and	ν (Zr=O)	ν(M-O) and
							$ν_s$(U=O)		*ν*(M-N)
Levo	3419mbr	-	1724vs	-	1620vs	-	-	-	-
Gly	-	3420br 3169m	1604vs	-	-	-	-	-	-
[Zn(Levo)(Gly)(H_2O)$_2$].10H_2O	3424mbr	3280sh 3100vw	-	1620vs	1593w	1336w	-	-	662w, 622vw, 507w
[ZrO(Levo)(Gly)(H_2O)].3H_2O	3418mbr	3260m 3140w	-	1625vs	1540ms	1337vw	-	812m	687vw, 642vw, 553vw, 501m
[La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O	3415mbr	3320sh 3180w	-	1620m	1577ms	1340vw	-	-	687w, 505w
[Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O	3416mbr	3300w 3120m	-	1621vs	1587vw	1340vw	-	-	684w, 595vw, 543vw, 501m
[UO_2(Levo)(Gly)].H_2O	3430mbr	3280sh 3100w	-	1620vs	1564vw	1340vw	919ms 813w	-	679m, 615vw, 547vw, 505w

Keys: s=strong, w=weak, m=medium, br=broad, *ν*=stretching

Electronic Spectra

The electronic absorption spectral data of the free ligands (Levo) and glycine (Gly) along with Zn(II), Zr(IV), La(III), Th(IV) and U(VI).complexes from 200 to 800 nm are shown in Figure 2. The electronic absorption spectra of Levo and Gly were absorbed at 249, 302, 309 nm and 290 nm, respectively (Table 3). The band at 249 nm may be attributed to π-π^* transition and the second bands at 302, 309 and 290 nm are assigned to n-π^* (-O-H, -C-O, -C-N and -C=O) transition, these transitions occur in case of unsaturated hydrocarbons which contain heteroatoms [24,25]. The intraligand bands were slightly shifted to longer wavelength (bathochromic shift) and to lower values (hypsochromic shift) upon complexation and the presence of new bands in the absorption spectra of all complexes indicated the formation of their metal complexes. The new bands in the range from 445 to 460 nm may be assigned to the ligand to metal charge-transfer.

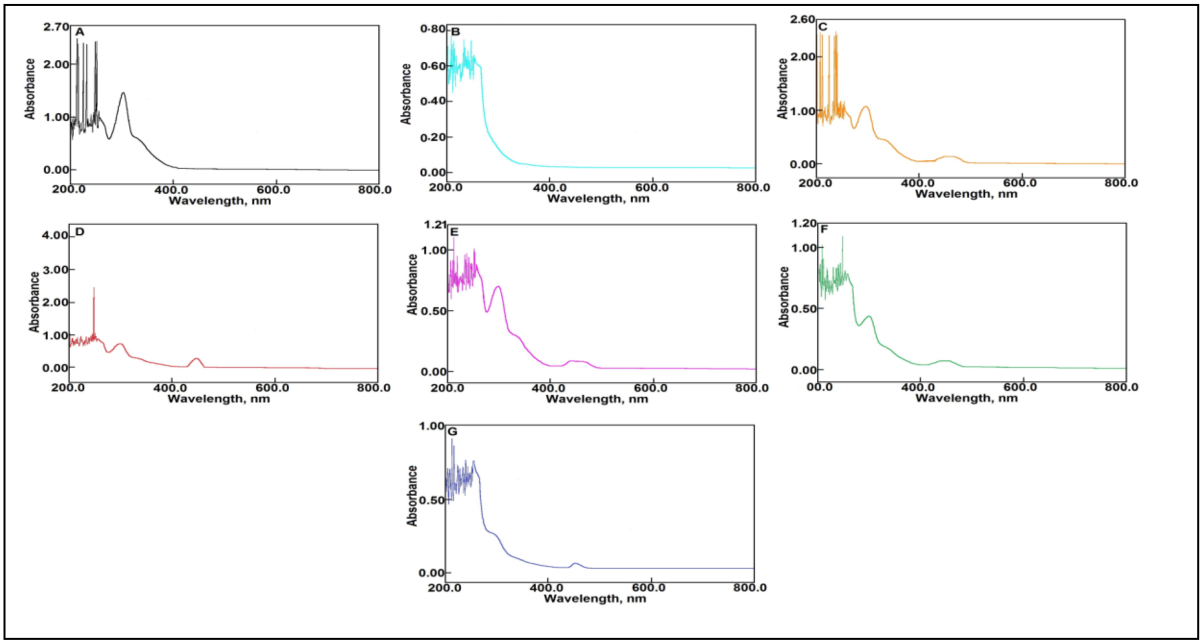


Figure 2: Electronic absorption spectra (A) Levo, (B) Gly, (C) [Zn(Levo)(Gly)(H_2O)$_2$].10H_2O, (D) [ZrO(Levo)(Gly)(H_2O)].3H_2O, (E) [La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O, (F) [Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O and (G) [UO_2(Levo)(Gly)].H_2O

Table 3: UV-Vis. spectra of Levo, Gly, Zn(II), Zr(IV), La(III), Th(IV) and U(VI)

Assignments (nm)	Levo	Mixed ligand complex with					
		Gly	Zn(II)	Zr(IV)	La(III)	Th(IV)	U(VI)
π-π^* transitions	249		255	248	250	252	240
						256	256
n-π^* transitions	302	290	296	298	298	299	284
	309		312	316	318	317	
Ligand-metal charge transfer	-	-	460	445	455	449	451

^{1}H NMR Spectra

The ^{1}H NMR spectra of Levo, Gly and thier metal complexes in DMSO-d$_6$ were measured (Figure 3) and analyzed to confirm the complexes formation. The ^{1}H NMR spectrum for Levo shows signals of the aromatic hydrogens in the range δ: 7.51-8.95 ppm (Table 4) and singlet signal at δ: 15.18 ppm for the carboxylic proton [24]. The chemical shift values for δ(-CH) of all complexes were only slightly changed. This small shift was expected as there was no hydrogen near the coordination sites. The signal proton for (-COOH) was not detected in the spectra of all complexes suggesting coordination of Levo and Gly through its carboxylato oxygen atom [26]. Also, the ^{1}H NMR spectra for the complexes exhibit new signal in the range, δ: 4.17-5.00 ppm due to the presence of water molecules in the complexes [27].

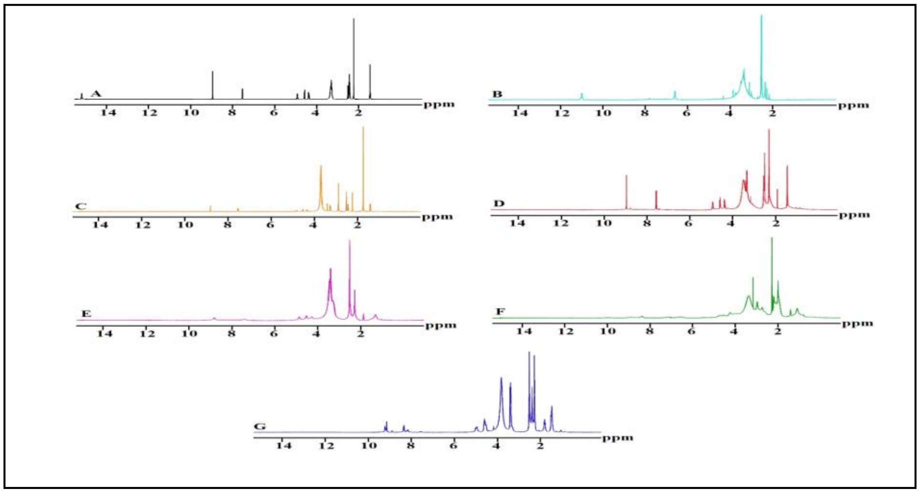


Figure 3: ^{1}H NMR spectra for (A) Levo, (B) Gly, (C) $[Zn(Levo)(Gly)(H_2O)_2].10H_2O$, (D) $[ZrO(Levo)(Gly)(H_2O)].3H_2O$ (E) $[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$, (F) $[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$ and (G) $[UO_2(Levo)(Gly)].H_2O$

Table 4: ^{1}H NMR values (ppm) and tentative assignments for (A) Levo, (B) Gly, (C) $[Zn(Levo)(Gly)(H_2O)_2].10H_2O$, (D) $[ZrO(Levo)(Gly)(H_2O)].3H_2O$ (E) $[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$, (F) $[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$ and (G) $[UO_2(Levo)(Gly)].H_2O$

A	B	C	D	E	F	G	Assignments
1.44–1.46	-	1.39-1.73	1.44-1.91	1.30-1.87	1.09-1.98	1.45-1.80	δH,-CH_3
2.23-2.51	2.26-2.99	2.23-2.88	2.30-2.55	2.28-2.51	2.17-2.96	2.26-2.51	δH, -NH_2
3.29-3.30	3.08-3.85	3.26-3.69	3.17-3.49	3.30-3.43	3.15-3.97	3.38-3.81	δH, -CH_2 aliphatic
-	-	4.32-4.83	4.36-4.94	4.28-4.86	4.23-4.72	4.17-5.00	δH, H_2O
7.51-8.95	-	7.52-8.81	7.55-8.96	7.43-8.82	7.12-9.93	8.13-9.21	δH, -CH aromatic
15.18	11	-	-	-	-	-	δH, -COOH

Thermal Studies

Thermogravimetric analyses (TG) and (DTG) of Levo, Gly and their complexes are used to get information about the thermal stability of these new complexes, decide whether the water molecules (if present) are inside or outside the inner coordination sphere of the central metal ion and to suggest a general scheme for thermal decomposition of these chelates. In the present investigation, heating rates were suitably controlled at 10°C min^{-1} under nitrogen atmosphere and the weight loss is measured from the ambient temperature up to ~1000°C. The TG and DTG curveof ligands and their complexes are shown in Figure 4 and the data are collected in Table 5. The weight loss for each chelate are calculated within the corresponding temperature ranges. These data support the proposed complexes chemical formulas. Decomposition of Levo ($C_{18}H_{20}N_3O_4F$) started at room temperature and finished at 1000°C with two stages. The first stage at 68°C with no weight loss associated to solid-solid interaction. The second stage at two maxima 341 and 531°C and is accompanied by a weight loss 100.0%, corresponding exactly to the loss of $8C_2H_2$+2CO+HF+O_2+N_2+NH_3 which very closely to calculated value 100.0%.

The TG curve of $[Zn(Levo)(Gly)(H_2O)_2].10H_2O$ complex exhibits three main degradation steps. The first decomposition step occurred at maximum temperature 79°C with a weight loss of 25.16%, which could be due to elimination of lattice water. The second step of decomposition occurred at one maximum temperature 308°C and is accompanied by a weight loss of 15.37%, corresponding to the loss of the two coordinated water molecules and glycine. The third step occurred at one maximum temperature 727°C and loses $8C_2H_2+2CO_2+0.5F_2+N_2+NH_3$ giving Zn as a final product. The TG curve of $[ZrO(Levo)(Gly)(H_2O)].3H_2O$ complex exhibits three main degradation steps. The first step of decomposition with one maximum temperature at 76°C and is accompanied by a weight loss of 8.81%, corresponding to the loss of $3H_2O$. The second step of decomposition occurred at three maxima 213, 299 and 402°C and is accompanied by a weight loss of 15.00%, corresponding to the loss of glycine and one water molecule. The third step of decomposition occurred at one maximum temperature 850°C and is accompanied by a weight loss of 44.35%, giving ZrO_2+6C as a thermally stable final product.

The TG curve of $[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$ complex exhibits two main degradation steps. The first step of decomposition occurred at one maximum temperature 78°C and is accompanied by a weight loss of 5.25% (calc. 5.29%), corresponding to the loss of $2H_2O$. The second step of decomposition occurred at four maxima 204, 297, 338 and 384°C and is accompanied by a weight loss of 16.12% (calc.16.17%), corresponding to the loss of $C_2H_4+NO_2+2H_2O$. The third step of decomposition occurred at one maximum temperature 875°C and is accompanied by a weight loss of 41.81% (calc.42.25%), corresponding to the loss of $5C_2H_2+CH_4+0.5F_2+0.5H_2O+NH_4Cl+2NO$ giving $LaO_{1.5}$+7C as a final product.

Thermogravimetric for $[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$ complex shows three weight loss events. The first step of decomposition occurred with a maximum temperature at 64°C corresponding to the loss of two water molecules of hydration. The second step of decomposition occured with a maximum temperature at 307°C corresponds to the loss of two water molecules and glycine. The third step of decomposition occurred with a maximum temperature at 852°C corresponds to the loss of $9C_2H_2+HF+Cl_2+N_2+NO_2$. There are three significant mass loss events due to the decomposition of ligand-metal molecules giving ThO_2 as a final product.

The TG curve of $[UO_2(Levo)(Gly)].H_2O$ complex exhibits three main degradation steps. The first step of decomposition occurred with one maximum temperature 73°C and is accompanied by a weight loss of 2.46%, (calc. 2.49%) corresponding to the loss of H_2O. The second step of decomposition occurred at one maximum temperature 300°C and is accompanied by a weight loss of 10.22%, (calc. 10.25%) corresponding to the loss of glycine. The third step of decomposition found at 860°C and accompanied to the loss of $8C_2H_2+2CO_2+0.5F_2+N_2+NH_3$ giving UO_2 as a final product. Loss of water of crystallization for the complexes at a relatively low temperature may indicate weak H-bonding involving the H_2O molecule. The decomposition mechanisms are only based on speculation and the thermal analysis without a complementary technique (gas chromatography). The suggested residues confirmed on the basis weight loss % calculation and IR for final product.

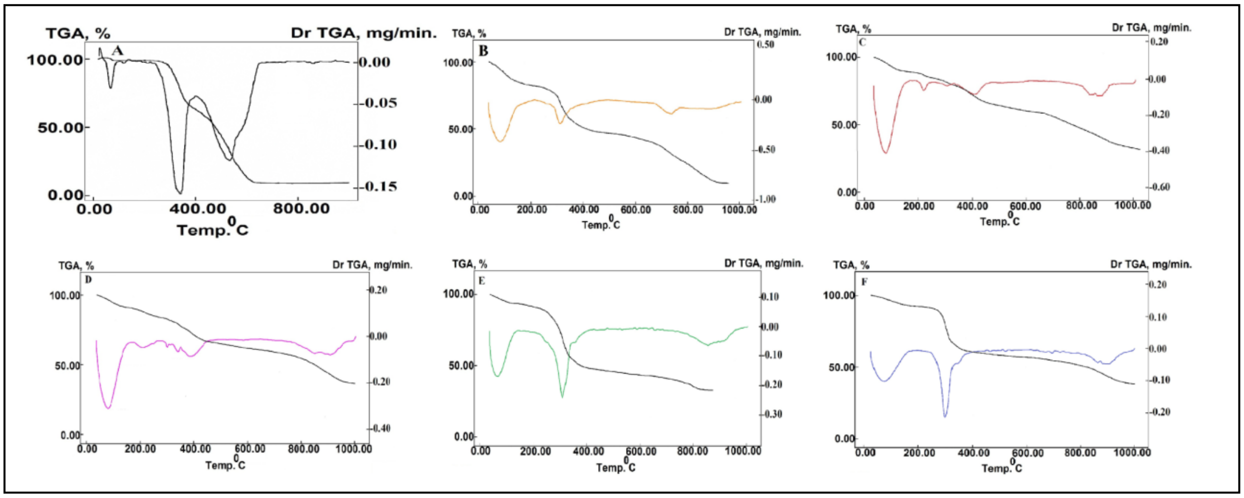


Figure 4: TGA and DTG diagrams for (A) Levo, (B) Gly, (C) $[Zn(Levo)(Gly)(H_2O)_2].10H_2O$, (D) $[ZrO(Levo)(Gly)(H_2O)].3H_2O$ (E) $[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$, (F) $[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$ and (G) $[UO_2(Levo)(Gly)].H_2O$

Table 5: The maximum temperature T_{max} (°C) and weight loss values of the Decomposition stage for Levo, Gly and their complexes

Compounds	Decomposition	T_{max}(°C)	Weight loss (%)		Lost species
			Calc.	Found	
Levo	First step	68			
($C_{18}H_{20}N_3O_4F$)	Second step	3,41,531	100	100	$8C_2H_2+2CO_2+HF+N_2+NH_3$
	Total loss		100, 0.0	100	
	Residue				
[Zn(Levo)(Gly)(H_2O)$_2$].10H_2O	First step	79	25.16	25.12	$10H_2O$
($ZnC_{20}H_{47}FN_4O_{18}$)	Second step	308	15.37	15.33	$C_2H_4+NO_2+2H_2O$
	Third step	727	50.33	52.46	$8C_2H_2+2CO_2+0.5F_2+N_2+NH_3$
	Total loss		90.86	90.91	
	Residue		9.14	9.09	Zn
[ZrO(Levo)(Gly)(H_2O)].3H_2O	First step	76	8.81	8.77	$3H_2O$
($ZrC_{20}H_{31}FN_4O_{11}$)	Second step	213, 299, 402	15	14.95	$C_2H_4+NO_2+H_2O$
	Third step	850	44.35	44.13	$5C_2H_2+CO+CO_2+0.5F_2+3NH_3$
	Total loss		68.16	67.85	
	Residue		31.84	32.15	ZrO_2+6C
[La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O	First step	78	5.29	5.25	$2H_2O$
($LaC_{20}H_{31}FN_4O_{10}Cl$)	Second step	204, 297, 338, 384	16.17	16.12	$C_2H_4+NO_2+2H_2O$
		875			
	Third step		42.25	41.81	$5C_2H_2+CH_4+0.5F_2+0.5H_2O+NH_4Cl+2NO$
	Total loss		63.71	63.18	
	Residue		36.29	36.82	$LaO_{1.5}+7C$
[Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O	First step	64	4.45	4.42	$2H_2O$
($ThC_{20}H_{31}FN_4O_{10}Cl_2$)	Second step	307	13.6	13.55	$C_2H_4+NO_2+2H_2O$
	Third step	852	49.31	49.28	$9C_2H_2+HF+Cl_2+N_2+NO_2$
	Total loss		67.36	67.25	
	Residue		32.64	32.75	ThO_2
[UO_2(Levo)(Gly)].H_2O	First step	73	2.49	2.46	H_2O
($UC_{20}H_{25}FN_4O_9$)	Second step	300	10.25	10.22	$C_2H_4+NO_2$
	Third step	860	49.86	49.17	$8C_2H_2+2CO_2+0.5F_2+N_2+NH_3$
	Total loss		62.6	61.85	
	Residue		37.4	38.15	UO_2

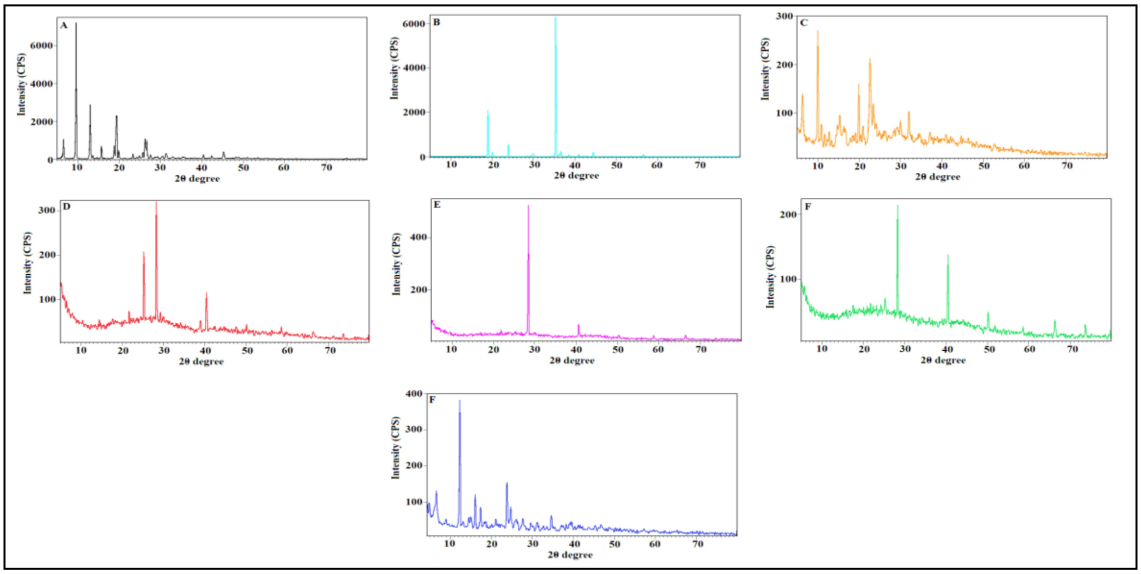


Figure 5: Powder XRD pattern for (A) Levo, (B) Gly, (C) [Zn(Levo)(Gly)(H_2O)$_2$].10H_2O, (D) [ZrO(Levo)(Gly)(H_2O)].3H_2O, (E) [La(Levo)(Gly)(H_2O)$_2$]Cl.2H_2O, (F) [Th(Levo)(Gly)(H_2O)$_2$]Cl_2.2H_2O and (G) [UO_2(Levo)(Gly)].H_2O

X-ray Diffraction

The X-ray diffraction method is a tool to distinguish crystalline from non-crystalline (amorphous) materials and give information about unit cell structure, Lattice Parameters and miller indices. Generally, the sharp, narrow and intense peaks suggest the high purity and crystallinity [28]. The crystal structures of the prepared compounds Levo, Gly and their complexes were characterized by X- ray diffraction and recorded over the scanning range 2θ = 10-70˚(Figure 5). The diffraction of Levo (Table 6), exhibited three diffraction peaks at 2θ [d value A°] = 9.64[9.17], 13.03[6.79] and 19.38[4.58]. The diffraction of Gly, exhibited three diffraction peaks at 2θ [d value A°] =19.01[4.67], 20.13[4.41], 35.39[2.54], 36.62[2.45]. The diffractogram of Zn(II) complex, indicated main peaks at 2θ [d value A°] = 9.99[8.85], 19.94[4.45], and 22.63[3.93]. The XRD patterns of Zr(IV) complex, exhibited peaks corresponding to 2θ [d value A°] = 25.25[3.53], 28.28[3.16] and 40.46[2.23]. The x-ray powder diffraction for La(III) complex, gives peaks at 2θ [d value A°] = 28.46[3.14], 40.60[2.22], 58.81[1.57] and 66.50[1.41].The diffraction Th(IV) complex , gives peaks at 2θ [d value A°] = 28.31[3.15], 40.49[2.23] and 50.15 [1.82].The XRD patterns of U(VI) complex, gives peaks at 2θ [d value A°] = 6.57[13.44], 12.28[7.21] and 23.78[3.74].

Table 6: The average crystallite size of Levo, Gly and thier complexes estimated from XRD pattern

Compounds	2θ (°)	d value (A°)	Relative intensity (%)
Levo	9.64	9.17	100
Gly	35.39	2.54	100
$[Zn(Levo)(Gly)(H_2O)_2].10H_2O$	9.99	8.85	100
$[ZrO(Levo)(Gly)(H_2O)].3H_2O$	28.28	3.16	100
$[La(Levo)(Gly)(H_2O)_2]Cl.2H_2O$	28.46	3.14	100
$[Th(Levo)(Gly)(H_2O)_2]Cl_2.2H_2O$	28.31	3.15	100
$[UO_2(Levo)(Gly)].H_2O$	12.28	7.21	100

CONCLUSION

The synthesis and characterization of five mixed ligand complexes with Zn(II), Zr(IV), La(III), Th(IV) and U(VI) have been synthesized with physicochemical and spectroscopic methods as well as thermal analyses. In all complexes, Levo acts as bidentate ligand bound to metal ion through pyridone oxygen and one carboxylate oxygen whereas Gly coordinate through nitrogen atom of amine group and one oxygen atom of carboxylic group.

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