

## Physicochemical and biological activity studies on complexes of some transition elements with mixed ligands of glycine and urea

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### ARTICLE INFO

#### Article history:

Received: August 8, 2018

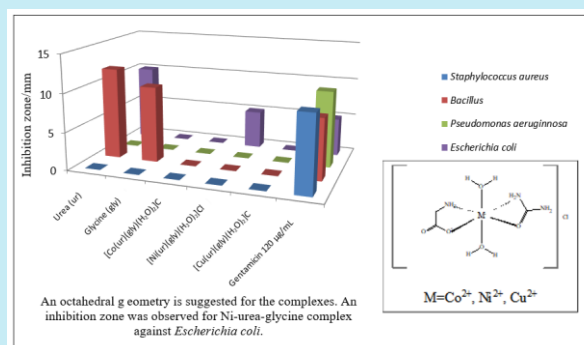
Accepted: November 11, 2018

Published: December 5, 2018

#### Keywords:

1. urea
2. glycine
3. transition elements
4. complexes

**ABSTRACT:** The reaction of urea (ur) and glycine (gly) with the metal ions Co(II), Ni(II) and Cu(II) in ethanolic solution of 1M:1L<sub>1</sub>:1L<sub>2</sub> molar ratio (where M= Co(II), Ni(II) and Cu(II), and L<sub>1</sub> = urea L<sub>2</sub> = glycine) led to the preparation of complexes of the general formula [M(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl. Elemental microanalysis (CHN), molar conductivity measurements, IR, <sup>1</sup>HNMR, Mass and UV-VIS spectroscopic, and magnetic susceptibility measurements were used for the characterization of the compounds. Thermal analyses were used for the complexes degradation characterization. The complexes have an octahedral geometry and are of electrolytic nature in DMSO solvent with the absence of inner-sphere coordination of the chloride anion. An inhibition zone was observed for Ni-urea-glycine complex against *Escherichia coli* when the biological activity was considered.



### 1. Introduction

The synthesis and study of mixed ligand transition metal complexes have been of growing interest<sup>1, 2</sup>. New materials with useful properties such as electrical conductivity photoluminescence, magnetic exchange, nonlinear optical property and antimicrobial activity can be provided by using mixed ligand transition metal complexes<sup>3-5</sup>.

Urea (CO(NH<sub>2</sub>)<sub>2</sub>) plays an important role in many biological processes such as decomposition of proteins and amino acids catabolism. In 1828, Wöhler discovered urea, when organic materials were prepared from inorganic substances.

All living things contain building blocks of amino acids<sup>6</sup>, which were first discovered as constituents of natural products and then observed to be the major components of proteins.

All life forms on earth consist of the simplest proteinaceous amino acid, called glycine or amino acetic acid<sup>7</sup>. Glycine is a neutral, aliphatic, optically inactive nonessential amino acid<sup>8</sup> and it is the only protein amino acid that does not have optical isomers<sup>9</sup>. Most of the metal ions form mono, bis and tris complexes with glycine that acts as a bidentate ligand forming stable 5-membered chelating rings via the N atom of the amino group and O atom of carboxylate group<sup>10</sup>.

The mixed ligand complexes of urea and glycine acid with Co(II), Ni(II) and Cu(II) ions were synthesized, characterized and thermally studied for the first time in this work.

### 2. Materials and methods

#### 2.1 Materials



All Chemical reagents used were purchased from BDH and used as provided.

## 2.2 Synthesis of the complexes

Generally, the solid complexes were prepared by the same methodology previously described<sup>11</sup>. Briefly, an ethanolic solution of hydrated metal chloride (0.01 mol) was dropwise added in an ethanolic solution of the first ligand (urea 0.01 mol) with stirring. The mixture was refluxed for 12 h with constant stirring. A hot solution of 0.01 mol glycine in 1:1 ethanol / water mixture ratio was dropwise added to the urea / metal mixture and drops of 1 mol L<sup>-1</sup> NaOH solution were used to adjust pH 7.0 - 7.5 to deprotonate NH<sub>3</sub><sup>+</sup> of the glycine to NH<sub>2</sub>. The mixture was refluxed for 2 h until resulting in the formation of a colored precipitate. The resulting product was filtered off and then washed with distilled water to remove NaCl. The product was further washed with absolute ethanol/dimethylformamide (DMF) and left to dry. Acceptable yield percentage was obtained (52-66%).

## 2.3 Instrumentation

Glass capillary tubes were used to measure the melting points of the metal complexes in degrees celsius on a Stuart Scientific electrothermal melting point apparatus. Silica Gel GF<sub>254</sub> plates (mn-kieselgel G., 0.2 mm thickness) was used for TLC. Vario ELFab instrument was used for elemental analysis (carbon, hydrogen and nitrogen) of complexes. Chloride was volumetrically or gravimetrically determined by silver nitrate. The amount of water was determined gravimetrically using weight loss method and also from thermal analysis. Perkin-Elmer 2380 flame atomic absorption spectrophotometer was used to measure the metal content. Jenway conductivity meter model 4510 was used to measure the molar conductance of 10<sup>-3</sup> mol L<sup>-1</sup> solutions of the metal complexes in dimethylsulfoxide (DMSO) solvent. IR spectra of the metal complexes were measured

by using FT/IR-140 (Jasco, Japan). A Varian FT-300 MHz spectrometer in d<sub>6</sub>-DMSO solvent was used for obtaining proton <sup>1</sup>H NMR spectra, using TMS as internal standard. Mass spectra were recorded on a JEOL JMS600 spectrometer. The electronic spectra of the complexes were measured in the range 400-800 nm using an UV-VIS spectrophotometer Specord 200, Analytik Jena (Germany). The mass susceptibility ( $\chi_g$ ) of the solid complexes was measured at room temperature using Gouy's method on a magnetic susceptibility balance from Johnson Metthey and Sherwood model. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) were performed using the Shimadzu DTA-50 and Shimadzu TGA-50H thermal analyzers. The experiments were carried out in the temperature range from 25 to 800 °C under nitrogen atmosphere in a platinum pan, heating rate of 10 °C / min and flow rate of 30 mL min<sup>-1</sup>. The antibacterial activity against four species of bacteria (*Staphylococcus aureus*, *Bacillus* spp., *Escherichia coli* and *Pseudomonas aeruginosa*) was tested by agar diffusion method. 1000 µg mL<sup>-1</sup> concentration for each of these compounds were individually prepared in DMSO, then the filter paper disc (whatman No.1.5 mm diameter) was saturated with the solution of these compounds. The discs were placed on the surface of Millar Hinton agar dishes seeded with the strains of bacteria. The inhibition zones (mm) were measured after 24 h at 37 °C. DMSO and gentamicin (120 µg mL<sup>-1</sup>) were used as control and reference, respectively.

## 3. Results and discussion

Complexes of Co(II), Ni(II) and Cu(II) with urea (ur) and glycine (gly) ligands have been prepared and characterized. Analytical data, physical properties, molar conductivity, and composition of the synthesized complexes are given in [Tables 1](#) and [2](#). The molar conductivity values (135-149 S cm<sup>2</sup> mol<sup>-1</sup>) reflect the electrolytic properties of these complexes. The single spot appearance in the TLC proves the purity of these complexes.

**Table 1.** Some physical properties of the complexes.

Complex Proposed Formula	Color	M.p / °C	TLC		molar conductivity $\Lambda_m / S\ cm^2\ mol^{-1}$
			No.of spots	Rf	
[Co(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Co(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	dark violet	>350	One	0.28	149
[Ni(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Ni(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	pale green	226±1	One	0.39	135
[Cu(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Cu(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	light blue	>350	One	0.39	148

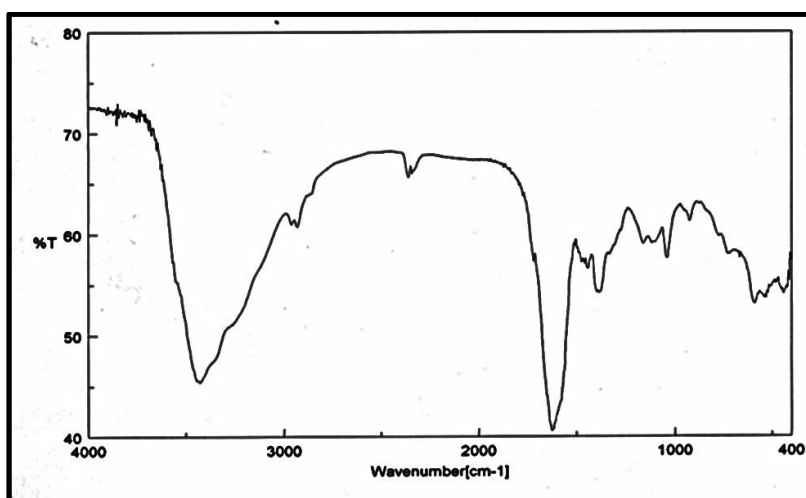
**Table 2.** Elemental analysis of the complexes.

Complex proposed formula	Molar mass		Elemental analysis									
			%C		%H		%N		%M		%Cl	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
[Co(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Co(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	264.53	264.03	13.62	13.65	4.57	4.58	15.89	15.91	22.28	22.32	13.40	13.45
[Ni(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Ni(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	264.29	264.34	13.63	13.63	4.58	4.58	15.90	15.90	22.21	22.20	13.41	13.43
[Cu(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl [Cu(C <sub>3</sub> H <sub>12</sub> N <sub>3</sub> O <sub>5</sub> )]Cl	269.14	269.19	13.38	13.39	4.49	4.49	15.61	15.61	23.61	23.61	13.17	13.17

### 3.1 IR spectra of urea - glycine complexes

The coordination sites of urea and glycine ligands in their complexes were investigated. The infrared spectra show that urea acts as a neutral bidentate ligand through C=O and NH<sub>2</sub> groups while glycine behaves as a bidentate anion ligand

through COO<sup>-</sup> and NH<sub>2</sub> groups. IR spectra of urea-glycine complexes are represented in Figures 1, 2 and 3. Assignments of the characteristic bands are summarized in Table 3. As it was postulated, the metal complexes were quite different when compared with the free ligands.

**Figure 1.** IR spectrum of [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex.

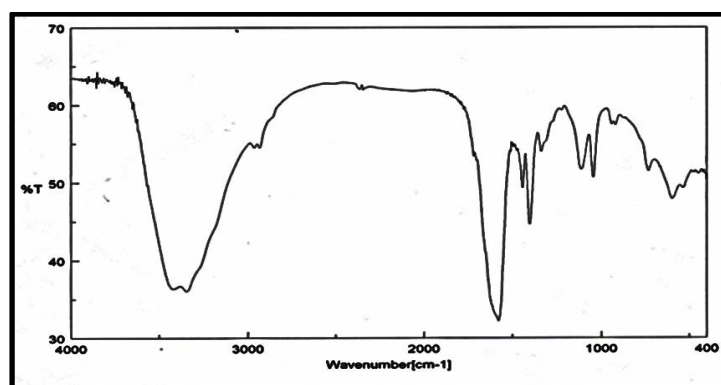


Figure 2. IR spectrum of [Ni(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex.

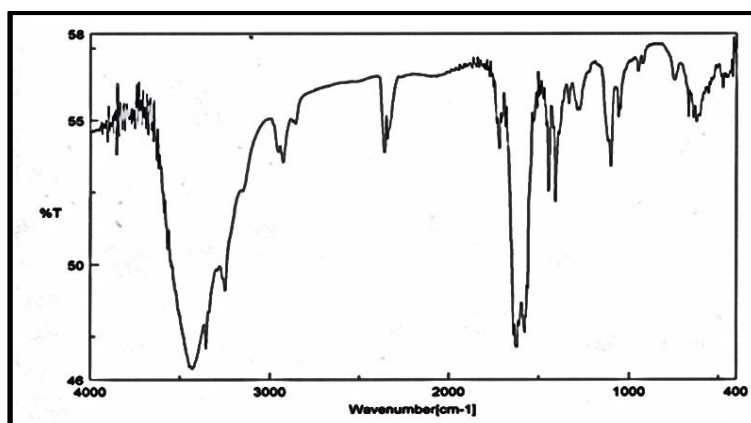


Figure 3. IR spectrum of [Cu(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex.

**Table 3.** Main IR bands ( $\text{cm}^{-1}$ ) of the urea-glycine complexes

Urea	Glycine	[Co(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	[Ni(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	[Cu,(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	Assignment
-	3164-3007br	-	-	-	$\nu(\text{NH}_3^+)$
3353m	-	ur-3250br gly-3185w.br	ur-3270br gly-3168w.br	ur-3248br gly-3160br	$\nu_s(\text{NH}_2)$
3466 m	-	ur, gly - 3376br	ur.gly - 3346m	ur - 3355 m gly -3290w	$\nu_{as}(\text{NH}_2)$
1618br	-	-	-	1609w	$\delta$ (NH)
-	1410m	1397 m	1402s	1408s	$\nu_s(\text{COO}^-)$
-	1598br	1509w	1578s	1578m	$\nu_{as}(\text{COO}^-)$
1695w	1715w	ur - 1625s gly -1718m	ur - 1680w gly -1718w	ur - 1618 m gly-1719m	$\nu(\text{CO})$
1468br	1033s	ur - 1474w gly -1040m	ur - 1475w gly -1045m	ur-1475w gly -1050 w	$\nu(\text{CN})$
-	2892br	2885br	2863 w.br	2857br	$\nu(\text{CH}_2)$
-	1442m	1439m	1441s	1446s	$\delta$ (CH <sub>2</sub> )
-	-	3431br	3422br	3432br	H <sub>2</sub> O $\nu(\text{OH})$
-	-	451w	483 w	475 w	$\nu(\text{M-O})$
-	-	440w	460 w	421 w	$\nu(\text{M-N})$

s = strong, m = medium, br = broad, w = weak, w.br = weak and broad

The infrared spectral data of the complexes are as follows:

(1) All the complexes spectra show a broad band at 3422-3432  $\text{cm}^{-1}$  that corresponds to the stretching mode of water existing in the complexes as identified by thermal and elemental analysis. The coordinated water is identified by the appearance of  $\rho_r$  (rocking) and  $\rho_w$  (wagging) at 925  $\text{cm}^{-1}$  and 511  $\text{cm}^{-1}$ , respectively<sup>12</sup>.

(2) The amino groups of urea show lower-shift of 123-103  $\text{cm}^{-1}$  and of 120-90  $\text{cm}^{-1}$  for symmetrical and asymmetrical stretching  $\nu(\text{NH}_2)$  frequencies, respectively. This strongly suggests that the nitrogen atom of amino group must be involved in complexation, and the appearance of a new band in the range of 406-460  $\text{cm}^{-1}$ , assigned to  $\nu(\text{M-N})$  vibration, confirms this proposition<sup>13,14</sup>.

(3) A new band at 1680-1618  $\text{cm}^{-1}$  is attributed to  $\nu(\text{CO})$  from urea, assigned to  $\nu(\text{C=O-M})$ .

(4) The characteristic bands in complexes spectra occur in the ranges 3185-3160  $\text{cm}^{-1}$  and 3376-3290  $\text{cm}^{-1}$  for symmetrical and asymmetrical  $\nu(\text{NH}_2)$  group of glycine, respectively, which appears at lower wave number than the free  $\nu(\text{NH}_2)$ . Hence, coordination through nitrogen of the amino group is involved<sup>15</sup>.

(5) The symmetrical  $\nu(\text{COO}^-)$  and asymmetrical  $\nu(\text{COO}^-)$  vibrations of glycine shift by 13-8  $\text{cm}^{-1}$  and 89-20  $\text{cm}^{-1}$ , respectively. This confirms that carboxylate is acting as a monodentate group<sup>16</sup>. Glycine acts as monobasic bidentate, through the nitrogen of amino and oxygen of carboxylate groups in these complexes<sup>17,18</sup>.

(6) The IR spectra in the range 483-451  $\text{cm}^{-1}$  and 460-421  $\text{cm}^{-1}$  show bands of low intensity due to stretching vibrations of  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$ , respectively<sup>13,14</sup>.

### 3.2. <sup>1</sup>HNMR spectra of urea-glycine complexes

Complexes were investigated by using <sup>1</sup>HNMR spectra in d<sub>6</sub>-DMSO and TMS (tetramethyl silane) as standard and data are in Table 4. [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl, [Ni(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl and [Cu(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complexes show signals in the range 5.4-7.2 ppm attributed to the amide group of urea<sup>19, 20</sup>. The methylene group of glycine (-CH<sub>2</sub>-) in Co(II), Ni(II) and Cu(II) complexes absorbs near 3.2, 3.2 and 3.1 ppm, respectively. NH<sub>2</sub> group shows signals at 2.9, 2.5 and 2.6 ppm, respectively<sup>21, 22</sup>. In urea, one amine and the carbonyl groups are coordinated to the central metal ion without displacement of NH<sub>2</sub> proton,

while in glycine presents a new signal in the range 2.5-2.9 ppm because of the deprotonation of  $\text{NH}_3^+$  to  $\text{NH}_2$ . The appearance of a new signal around 3.5-

3.8 ppm confirms the presence of water molecules in the complexes<sup>23</sup>.

**Table 4.** <sup>1</sup>HNMR chemical shift (ppm) of free urea and glycine ligands and of complexes.

System	(CH) <sub>α</sub> α=Alpha	NH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> (gly)	NH <sub>2</sub> (ur)	H <sub>2</sub> O
urea	-	-	-	6-7.5	-
glycine	3.5	8-7	-	-	-
[Co(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	3.2	-	2.9	5.4 <sub>(bonding)</sub> 6.4 <sub>(nonbonding)</sub>	3.8
[Ni(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	3.2	-	2.5	4.7 <sub>(bonding)</sub> 7.2 <sub>(nonbonding)</sub>	3.7
[Cu(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	3.1	-	2.6	5.5 <sub>(bonding)</sub> 7 <sub>(nonbonding)</sub>	3.5

### 3.3 Mass spectra of urea-glycine complexes

The mass spectra of Co(II), Ni(II) and Cu(II) complexes with urea and glycine reveal molecular ion peaks at m/z (calc. 264.53, found 264.03 (4%)), (calc. 264.29, found 264.34 (11%)) and (calc. 269.14, found 269.19 (9%)), respectively.

The molecular ion of [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex loses glycinate ( $\text{NH}_2\text{CH}_2\text{COO}^-$ ) ion and 2H<sub>2</sub> leaving an ion at m/z 185.67, which by its turn, loses H<sub>2</sub>O, Cl, CO, NH<sub>3</sub> and H<sub>2</sub> giving an ion at m/z 85.01.

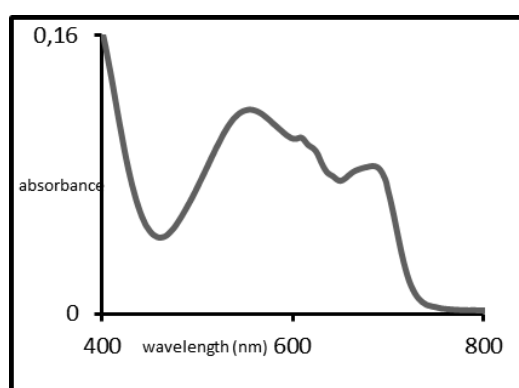
The mass spectrum of [Ni(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex exhibited a peak at m/z 244.90, indicating the loss of H<sub>2</sub> and NH<sub>3</sub>, then this molecular ion loses H<sub>2</sub>O and ½Cl<sub>2</sub> leaving an ion at m/z 192.83, which further loses one more H<sub>2</sub>NCH<sub>2</sub>COO<sup>-</sup> affording an ion at m/z 118.87. The complex [Cu(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl loses [CO, ½Cl<sub>2</sub>] and H<sub>2</sub>O to give ions at m/z 205.68 and 251.19, respectively.

### 3.4 Electronic and magnetic spectral analysis

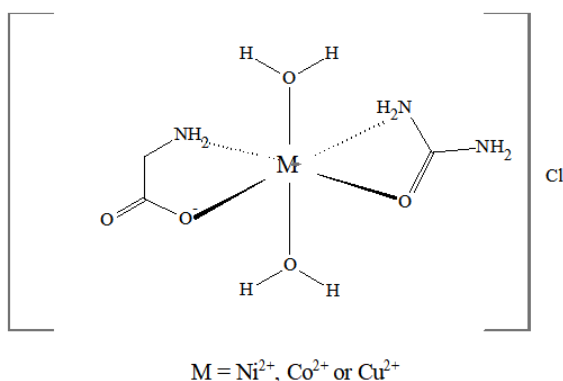
The magnetic moments of the Co(II), Ni(II) and Cu(II) complexes as well as their electronic spectra data have provided good evidence for the structures of these complexes as shown in Table 5. [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl hexa-coordination is suggested. This is based on the spectrum (Figure 5) recorded in DMSO solution which shows bands at 17985 cm<sup>-1</sup> and 14482 cm<sup>-1</sup>, due to transition of  $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}(\text{P})$  (ν<sub>3</sub>) and  $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$  (ν<sub>2</sub>), respectively<sup>23</sup>. The third band of the spectrum, assigned to ν<sub>1</sub>, could not be observed due to the limited range of the used instrument (200-1100 nm). [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl has a magnetic moments of 4.76 B.M; this value is due to a high-spin octahedral geometry around the Co(II) ion as reported previously<sup>24</sup>. Moreover, the violet colour of octahedral Co(II) complexes is in good agreement with those previously reported<sup>25</sup>.

**Table 5.** Magnetic moment and electronic spectral data in DMSO solution for the complexes.

complex	$\mu_{\text{eff}}$ / B.M	charge transfer bands / $\text{cm}^{-1}$	<i>d-d</i> transition bands / $\text{cm}^{-1}$	proposed structure
[Co(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	4.76	23697	17985, 14492	octahedral
[Ni(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	3.2	23419	21459, 14970, 13477	octahedral
[Cu(ur)(gly)(H <sub>2</sub> O) <sub>2</sub> ]Cl	1.43	24272	12987	distorted octahedral

**Figure 4.** UV-VIS spectrum of [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex in the MSO solution.

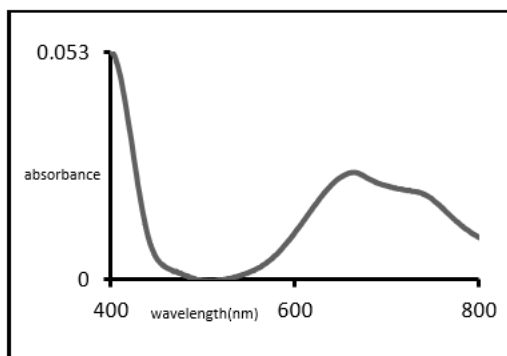
From the above discussion (Figure 5) of [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl can be suggested. Furthermore, previous studies proved that the broad bands centred at 23697  $\text{cm}^{-1}$  should be assigned to charge-transfer transitions in [Co(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl<sup>26</sup>.

**Figure 5.** Suggested structure for the complex.

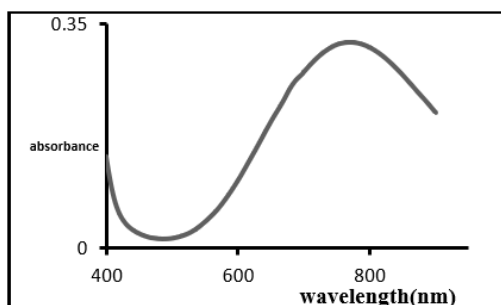
The magnetic moment data as well as the electronic spectrum data of the nickel complex are given in Table 5. The complex

[Ni(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl has a magnetic moment value of 3.2 B.M consistent with an octahedral geometry around the Ni(II) ion with a <sup>3</sup>A<sub>2g</sub> ground term, which lies in the range reported in the literature<sup>27</sup>. In addition, the complex has three bands in the UV-VIS recorded in DMSO solution (Figure 6): 21459  $\text{cm}^{-1}$  may be due to the <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (ν<sub>3</sub>); 14970  $\text{cm}^{-1}$  due to <sup>3</sup>A<sub>2g</sub> → <sup>3</sup>T<sub>1g</sub> (ν<sub>2</sub>); 13477  $\text{cm}^{-1}$  in the transition range of an octahedral structure around the Ni(II) ion (ν<sub>1</sub>) (Figure 5)<sup>28</sup>. The green colour is also an additional evidence for the octahedral structure<sup>26</sup>. The band at 23419  $\text{cm}^{-1}$  may be attributed to the charge transfer transition of [Ni(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex<sup>23</sup>.

[Cu(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl (structure in Figure 5) has an electronic spectrum (Figure 7) that shows a strong band at 12987  $\text{cm}^{-1}$  due to <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> transition, suggesting a distorted octahedral geometry<sup>26</sup>. The broadness in the band may be due to Jahn-Teller effect<sup>29</sup> and the proposed geometry is also supported by the blue colour of this complex<sup>27</sup>. The magnetic moment value of this complex 1.43 B.M agrees with the *d*<sup>9</sup> system containing one unpaired electron<sup>26</sup>. The observed band at 24272  $\text{cm}^{-1}$  in the spectrum of the complex may be due to LMCT (L → M charge transfer transition) of [Cu(ur)(gly)(H<sub>2</sub>O)<sub>2</sub>]Cl complex<sup>30</sup>.



**Figure 6.** UV-VIS spectrum of  $[\text{Ni}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$  complex in DMSO solution.



**Figure 7.** UV-VIS spectrum of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$  complex in DMSO solution.

### 3.5. Thermal analysis of Cu-urea-glycine complex

The thermal and kinetic parameters for each step in the decomposition sequences of the Cu-complex were determined by using the integral Coats-Redfern equation. The Coats-Redfern method is linearized for a correctly-chosen order of reaction ( $n$ ) and the activation energy ( $E_a$ ) is obtained from the slope of the  $\log [y]$  versus  $T^{-1}$  plot from Equation:

$$\log \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)} \right] = \log \left[ \frac{ZR}{qE_a} \left( 1 - \frac{2RT}{E_a} \right) \right] - \frac{E_a}{2.303RT} \text{ for } n \neq 1 \rightarrow 1$$

where:  $\alpha$  = fraction of mass loss,  $T$  = temperature (K),  $Z$  = pre-exponential factor,  $R$  = molar gas constant,  $q$  = heating rate and  $n$  = reaction order; estimated by Horovitz-Metzger method.

The thermodynamic parameters of the thermal degradation step: enthalpy ( $\Delta H^*$ ), entropy ( $\Delta S^*$ ), and Gibbs energy ( $\Delta G^*$ ) of activation are calculated using the following standard equations:

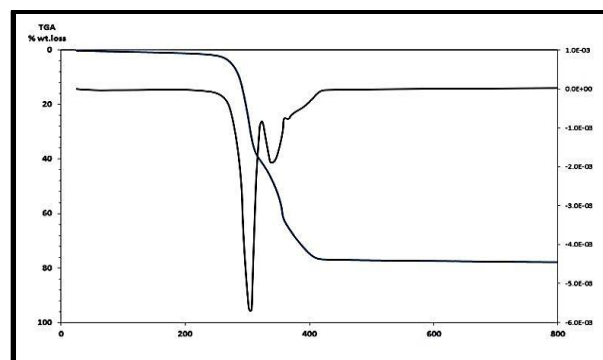
$$\Delta S^* = R \ln \frac{Zh}{kT_{\max}}$$

$$\Delta H^* = E_a - RT_{\max}$$

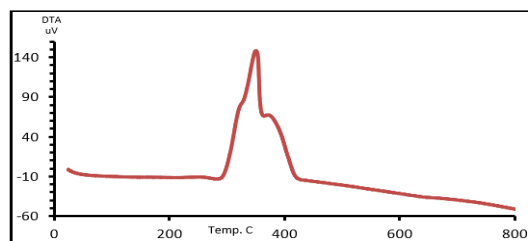
$$\Delta G^* = \Delta H^* - T_{\max} \Delta S^*$$

where  $z$ ,  $k$ , and  $h$  are the pre-exponential factor, Boltzmann and Planck constant, respectively.

The TG and DTA thermograms of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$  complex (Figures 8 and 9) are characterized by the three fast decomposition steps (25-318, 318-361 and 361-375 °C). The  $T_{\text{DTG}}$  at 302 °C is consistent with the evolution of 100% of coordinated water, 100% of bonded chloride and 60% the urea ligand (calc. 39.95%, found 39.93%). The activation energy calculated is 89 kJ mol<sup>-1</sup> (Table 6). The remaining urea molecule may be eliminated in the second step together with 52.72% of glycine molecule (calc. and found 23.43%). In this step (318-361 °C), the activation energy is 123 kJ mol<sup>-1</sup> and the order of decomposition reaction is 3.6 with the apparent  $T_{\text{DTG}}$  (334 °C) and the exothermic ( $T_{\text{DTA}}$ ) peak at 349 °C (Table 7). The third step, which corresponds to 17.57% loss of glycine molecule (calc. 4.86, found 4.84%) has an activation energy of 117 kJ mol<sup>-1</sup>. The final residue is CuO and 0.5C as ash [(O=21.6% gly, C=8.11% gly) (calc. and found 31.78%)]. The  $\Delta S^*$ ,  $\Delta H^*$  and  $\Delta G^*$  for these three steps are calculated (-119.3, -100.1 and -183.8 J K<sup>-1</sup> mol<sup>-1</sup>), (86.5, 120.2 and 114 kJ mol<sup>-1</sup>) and (122.5, 153.6 and 180.7 kJ mol<sup>-1</sup>), respectively.



**Figure 8.** TG and DTG curves of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$ .



**Figure 9.** DTA curve of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$ .



**Table 6.** Characteristic parameters of thermal decomposition ( $10\text{ }^{\circ}\text{C min}^{-1}$ ) for  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$ .

Comp.	Step	TGA				DTA		mass loss
		$\Delta m\%$ found (calc.)	$T_f/^\circ\text{C}$	$T_f/^\circ\text{C}$	$T_{DTG}$	$T_{DTA}$	Heat	
$[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$	1	39.93 (39.95)	25	318	3.2	323	exo	-[100% $\text{H}_2\text{O}$ + 100%Cl+60%ur]
	2	23.43 (23.43)	318	361	334	349	exo	-[40 %ur+52.72 % gly]
	3	4.86 (4.84)	361	375	363	368	exo	-[ 17.57% gly]
Final residue [(CuO +0.5C) (O=21.6%gly, C=8.11%gly)]: 31.78% (31.78%)								

**Table 7.** Kinetic and thermodynamic parameters of the thermal decomposition of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$ .

$[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$	1	0.9918	3.6	$3.7 \times 10^6$	3.2	89	-119.3	86.5	122.5
	2	0.9939	3.6	$4.1 \times 10^7$	334	123	-100.1	120.2	153.6
	3	0.9862	4.9	$1.9 \times 10^3$	363	117	-183.8	114	180.7

### 3.6. Antibacterial assay of synthesized complexes

Urea showed activity against the *Bacillus* spp. and *Escherichia coli* with inhibitory zones of 12 mm and 10 mm, respectively and glycine against the *Bacillus* with inhibitory zone of 9 mm. But no inhibition zone was observed for all the complexes against the four studied strains (*Bacillus* spp., *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus*) excepting the complex  $[\text{Ni}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$  which was active against *Escherichia coli* with inhibitory zone 5 mm. This is probably because urea denatures protein when dissolved, and for the presence of amino and carbonyl groups. However, after complexes formation there would be no activity, due to the coordination of the amino and carbonyl groups<sup>31</sup>.

### 4. Conclusions

The formulae and the stoichiometry of the complexes of urea and glycine with Co(II), Ni(II) and Cu(II) metal ions are suggested based on the analytical data and TGA results. Neutral bidentate behavior of the urea coordination through the amine nitrogen and carbonyl oxygen is identified by IR spectra. Glycine behaved as an anionic bidentate ligand through the carboxylate group and the neutral amino group. The electrolytic nature of the complexes was confirmed by the molar conductance values. All the complexes have an octahedral geometry, as revealed the spectral and magnetic results. The thermal decomposition studies of  $[\text{Cu}(\text{ur})(\text{gly})(\text{H}_2\text{O})_2]\text{Cl}$  allowed to access the kinetic parameters for the successive steps of its decomposition. The complexes have no

antibacterial activities against the four strains of bacteria, except the Ni-complex, which is active against *Escherichia coli*, probably due to protein denaturation.

## 5. Acknowledgments

Authors are grateful to Professor Hussein Al-Maydama for his valuable assistance.

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