

ARTICLE

Synthesis and Characterization of Co^{II}, Ni^{II} and Cu^{II} Complexes with Mixed Ligands of Histidine and Urea

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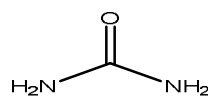
Abstract: Mixed ligand complexes of the type [ML₁L₂(H₂O)_n]Cl (where M= Co^{II}, Ni^{II} and Cu^{II}, L₁=urea and L₂=histidine) have been synthesized by the reactions of anhydrous metal chlorides with the two ligands in 1:1:1 molar ratios. The resulting complexes have been characterized by elemental analysis, molar conductivity measurement, IR, mass, electronic spectra, magnetic susceptibility measurements, in addition to thermal analysis. The molar conductance values ranging from 103.22 to 128.94 cm²mol⁻¹Ω⁻¹ show that these complexes are of electrolytic nature (in DMSO solvent) and clearly indicate the non-coordination of the anion chloride with the metal ions. The spectral data show that the complexes with Ni^{II} and Cu^{II} are of octahedral structure, whereas Co^{II} is square-planar. Unfortunately, the biological screening of these complexes showed no activity against the four studied strains, i.e., *Staphylococcus aureus* (TCC 29737), *Bacillus subtilis* (ATCC 6633), *Escherichia coli* (ATCC 11303) and *Pseudomonas aeruginosa* (ATCC 25619).

Keywords: Urea, Histidine, IR, ¹HNMR, Mass, UV, Thermal, Antibacterial Activity.

Introduction

In recent years, there has been renewed interest in the synthesis and study of mixed ligand transition metal complexes^[1,2], because they can provide new materials with useful properties, such as magnetic exchange, electrical conductivity, photoluminescence, nonlinear optical property and antimicrobial activity^[3-8].

Carbamide, carbonyldiamide or the most famous name urea CO(NH₂)₂ (Structure 1) plays an important role in many biological processes. The human body produces 20–30g of urea per day. In 1828, Wöhler discovered urea by evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate^[9].

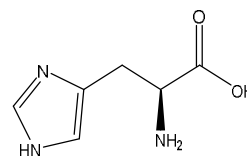


Structure 1

Amino acids are the major building blocks of all forms of life^[10]. Amino acids were earlier

discovered as constituents of natural products even before they were recognized as components of proteins.

Histidine or 2-amino-3-(1H-imidazol-4-yl) propanoic acid (Structure 2) is one of the naturally occurring essential amino acids and is often found at the active site of proteins^[11].



Structure 2

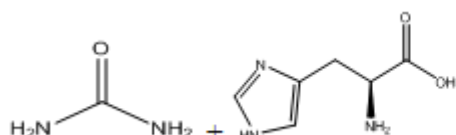
Literature survey shows that no studies on the synthesis and characterization of mixed ligand complexes of urea and histidine have been reported. Hence, the present paper reports on the preparation, coordination and structure of new mixed ligand Co^{II}, Ni^{II} and Cu^{II} complexes formed with urea and histidine.

Materials and Methods

Chemicals

All chemicals, such as solvents and metal (II) chlorides (i.e, Cobalt (II) chloride hexahydrate, Nickel (II) chloride hexahydrate and Copper (II) chloride dihydrate) were commercially available from BDH (British Drug House; a chemical company) and were used without further purification. Bacterial strains used in the study were: (*Bacillus subtilis*(ATCC 6633), (*Escherichia coli* (ATCC 11303),*S. aureus* ATCC 29737) and (*P. aeruginosa* (ATCC 25619). All the tested strains were reference strains and were obtained from the Department of Biology/Division of Microbiology and the Department of Food Sciences and Technology at Sana'a University.

Synthesis of Mixed Ligand Complexes



Instrumentation

Stuart Scientific electrothermal melting point apparatus was used to measure the melting points of the metal complexes at the Faculty of Science, Sana'a University. TLC was carried out on Silica Gel GF₂₅₄ plates (mn-kieselgel G., 0.2 mm thick) at Cairo University, Egypt. Carbon, hydrogen and nitrogen analyses for complexes have been carried out by Vario ELFab at Central Laboratory, Ain Shams University, Egypt.

Chloride was determined gravimetrically by silver nitrate and water percentage was determined gravimetrically using weight loss method at the Faculty of Science, Sana'a University.

The metal content was measured using Perkin-Elmer 2380 flame atomic absorption spectrophotometer at the central lab of the Ministry of Oil, Sana'a, Yemen.

The molar conductance of 10⁻³M solutions of the metal complexes in DMSO solvent was measured with Jenway conductivity meter model 4510 at the Faculty of Science, Sana'a University.

IR spectra of the metal complexes were measured by using (FT/IR – 140, Jasco, Japan) at the Faculty of Science, Sana'a University.

Generally, the solid complexes were prepared by adding dropwise an ethanolic solution of hydrated metal (II) chlorides (0.01mol) to an ethanolic solution of urea (0.01mol) with stirring. The mixture was refluxed for 12 hours with constant stirring; then, a hot solution of ethanol and water with 1:1 ratio of histidine (0.01mol) and drops of sodium hydroxide solution (1M) were added dropwise in order to adjust pH at 7-7.5 to deprotonate NH₃⁺ in the histidine and convert it into NH₂. The mixture was refluxed for 2 hours until colored precipitates formed. All material solutions were in 1:1:1 molar ratios. The resulting precipitates were filtered off and washed with cool distilled water to remove NaCl, followed by adding absolute ethanol till the solution became clear. After that, the precipitates were washed by DMF and left to dry^[12].

Mass spectra of the complexes were recorded on JEOL JMS600 spectrometer at Assiut University Central Lab., Egypt.

The electronic spectra of the complexes were measured in the range 400 – 800 nm by using UV-VIS spectrophotometer (specord200, Analytik Jena, Germany) at the Faculty of Science, Sana'a University.

The mass susceptibility (X_g) of the solid complexes was measured at room temperature using Gouy's method by a magnetic susceptibility balance of Johnson Metthey and Sherwood model at Cairo University Central Lab.

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) experiments were conducted using Shimadzu DTA-50 and Shimadzu TGA-50H thermal analyzers, respectively, at Micro-analytical Center Lab., Cairo University, Egypt.

The antimicrobial activity of the ligands and their metal complexes was tested against four species of bacteria (*Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa*) using filter paper disc method at the Faculty of Science, Sana'a University. The screened compounds were dissolved individually in DMSO in order to

make up a solution of 1000 µg/ml concentration for each of these compounds. Filter paper discs (Whatman No.1, 5 mm diameter) were saturated with the solution of these compounds. The discs were placed on the surface of solidified Millar Hinton agar dishes seeded by the tested bacteria. The diameters of inhibition zones (mm) were measured at the end of an incubation period, which was 24hrs at 37°C Discs saturated with DMSO are used as solvent control. Gentamicin of 120 µg/ml concentration was used as a reference substance for bacteria^[13].

Results and Discussion

The synthetic Co^{II}, Ni^{II} and Cu^{II} with urea and histidine complexes are investigated. Some physical properties, molar conductivity, analytical data and their composition are summarized in Tables (1 and 2). The elemental analysis shows that the formed complexes of Co^{II}, Ni^{II} and Cu^{II} with urea and histidine are of 1:1:1 (metal:u:his) molar ratio.

Table 1. Some physical properties of the complexes

Complex proposed formula	Color	M.p. °C	Yield %	TLC		molar conductivity Λ_m $\text{cm}^2\text{mol}^{-1}\Omega^{-1}$
				No. of spots	R _f	
[Co(u)(his)(H ₂ O)]Cl [Co(C ₇ H ₁₄ N ₅ O ₄)]Cl	dark violet	310	48.21	One	0.14	128.94
[Ni(u)(his)(H ₂ O) ₂]Cl [Ni(C ₇ H ₁₆ N ₅ O ₅)]Cl	green	>350	44.11	One	0.19	103.22
[Cu(u)(his)(H ₂ O) ₃]Cl [Cu(C ₇ H ₁₈ N ₅ O ₆)]Cl	brown	>350	70.29	One	0.21	119.53

Table 2. Some physical properties 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(u)(his)(H ₂ O)]Cl [Co(C ₇ H ₁₄ N ₅ O ₄)]Cl	326.60	326.68	25.74	25.73	4.32	4.32	21.44	21.44	18.04	18.04	10.86	11.87
[Ni(u)(his)(H ₂ O) ₂]Cl [Ni(C ₇ H ₁₆ N ₅ O ₅)]Cl	344.37	344.41	24.41	24.41	4.83	4.68	20.34	20.33	17.04	17.04	10.30	10.31
[Cu(u)(his)(H ₂ O) ₃]Cl [Cu(C ₇ H ₁₈ N ₅ O ₆)]Cl	367.25	368.30	22.89	22.83	4.94	4.93	19.07	19.04	17.30	17.30	9.65	9.64

M.p. = Melting point.

R_f = Retention Factor in Thin Layer Chromatography.

IR Spectra of Urea–Histidine Complexes

The infrared spectral data in Table 3 show that urea acts as a mono- or bidentate through $\nu(\text{C}=\text{O})$ or through two $\nu(\text{NH}_2)$ groups, while histidine acts as anion bidentate molecule, through $\nu(\text{COO}^-)$ and $\nu(\text{NH}_2)$ groups, suggesting that one metal is coordinated with two ligand molecules, urea and histidine.

The presence of a broad band at 3409–3432 cm^{-1} and another one of weak intensity in the region 895–572 cm^{-1} is ascribed to the stretching and deformation vibration of water.

In complexes of Co^{II} and Cu^{II}, urea acts as monodentate through $\nu(\text{CO})$, resulting in an increase of the $\nu(\text{CN})$ stretching frequency with

a simultaneous decrease in the $\nu(\text{CO})$ stretching frequency, but with no appreciable change in $\nu(\text{NH}_2)$ stretching frequency^[14,15].

In complex of Ni^{II}, urea acts as bidentate through two $\nu(\text{NH}_2)$ groups. This results in an increase of the $\nu(\text{CO})$ stretching frequency with a decrease of $\nu(\text{CN})$ stretching frequency, while the $\nu(\text{NH}_2)$ stretching frequencies would be shifted to lower values^[16].

The $\nu(-\text{NH}_3^+)$ band at 3010 cm^{-1} , which is characteristic for the zwitter ion, disappeared in the spectra of the complexes, because of being deprotonated to NH_2 in the complexes giving higher wave numbers in the spectra of the complexes by (70–27) cm^{-1} and (175–120) cm^{-1} ,

symmetrical and asymmetrical, respectively. This indicates that the $\nu(\text{NH}_2)$ group must be involved in coordination^[17-22].

The $\nu_{\text{symmetrical}}(\text{COO}^-)$ mode of histidine observed at 1414 cm^{-1} and $\nu_{\text{asymmetrical}}(\text{COO}^-)$ band observed at 1598 cm^{-1} are shifted to higher wave number, ($25\text{-}7\text{ cm}^{-1}$ and $30\text{-}19\text{ cm}^{-1}$) respectively in the spectra of complexes, indicating the coordination of carboxylic group *via* oxygen with metal^[17-22].

Other low intensity bands observed in the far IR region in the range $475\text{--}473\text{ cm}^{-1}$ and range

$432\text{--}417\text{ cm}^{-1}$ were assigned to $\nu(\text{M-O})$ and $\nu(\text{M-N})$ stretching vibrations, respectively^[23,24]. Other bands of ligands and their complexes are listed in Table 3.

Mass Spectra of Urea - Histidine Complexes

The mass spectra of Co^{II} , Ni^{II} and Cu^{II} complexes with urea and histidine showed molecular ion peaks at m/z (cal. 326.60, found 326.68 (15%)), (cal. 344.37, found 344.41(14%)) and (cal. 367.25, found 368.30 (100%)), respectively.

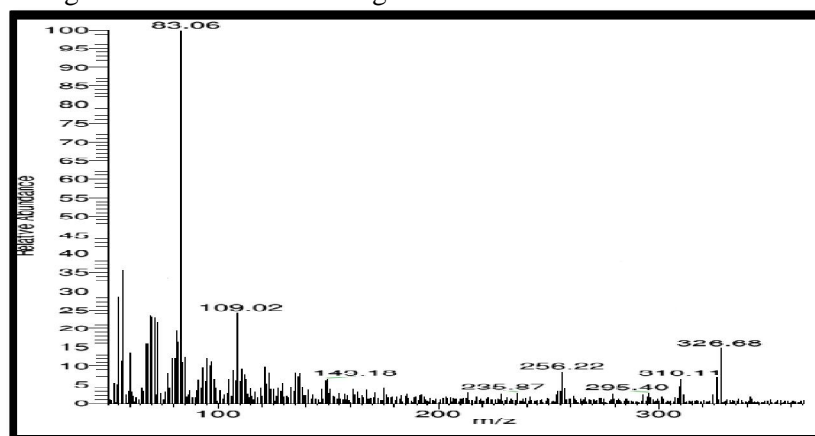


Figure 1. Mass spectrum of $[\text{Co}(\text{u})(\text{his})(\text{H}_2\text{O})]\text{Cl}$ complex.

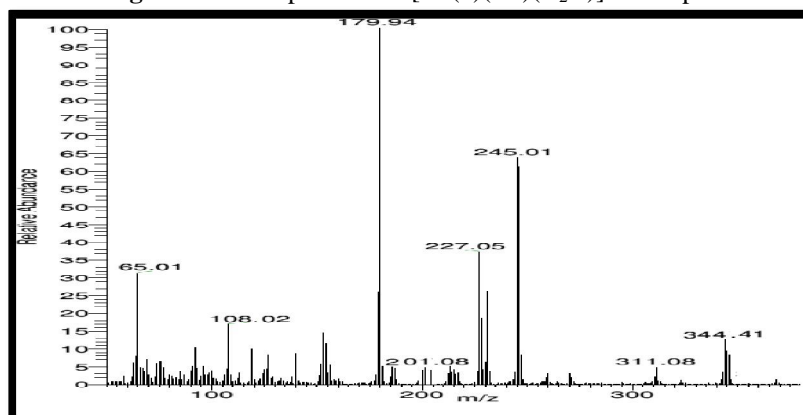


Figure 2. Mass spectrum of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ complex.

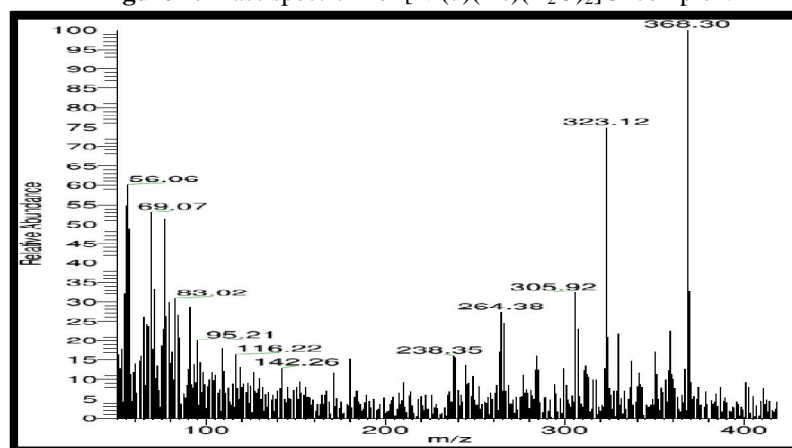


Figure 3. Mass spectrum of $[\text{Cu}(\text{u})(\text{his})(\text{H}_2\text{O})_3]\text{Cl}$ complex

Table 3. Significant IR spectral bands (cm^{-1}) of urea and histidine complexes

Assignment	$\nu(\text{NH}_3^+)$	$\nu_s(\text{NH}_2)$ $\nu(\text{H}_2\text{O})$ $\nu(\text{OH})$	$\nu_{as}(\text{NH}_2)$	$\nu(\text{NH}^b)$	$\nu_s(\text{COO})$	$\nu_{as}(\text{COO})$	$\nu(\text{CO})$	$\nu(\text{C-N})$	$\nu(\text{N-C})$	$\nu(\text{CH}_2)$	$\nu(\text{CH}_2)^b$	$\nu(\text{C-H})$	$\nu(\text{CH})$	$\nu(\text{CH})^b$	$\nu(\text{N=C})$	$\nu(\text{C=C})$	$\nu(\text{NH})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
[Cu(u)(his) (H_2O) ₃]Cl	-	U- 3264 ^{w,br} (His)3080 ^m	U- 3433 ^{br} (His)3170 ^{w,br}	1636 ^w	1421 ^m	1617 ^s	U-1653 ^w (His)1733 ^w	U-1475 ^w (His)1078 ^s	1115 ^m	2878 ^m	1458 ^w	3030 ^{w,br}	2927 ^m	1272 ^m	1636 ^w	1543 ^w	2960 ^m	473 ^w	432 ^w
[Ni(u)(his) (H_2O) ₂]Cl	-	U-3250 ^{w,br} His- 3080 ^m	U-3390 ^{w,br} His-3185 ^{w,br}	1622 ^w	1439 ^s	1617 ^w	U-1700 ^w His-1721 ^w	U-1458 ^w His-1078 ^s	1117 ^m	2856 ^{br}	1458 ^w	3033 ^{w,br}	2926 ^m	1271 ^s	1635 ^w	1538 ^w	2959 ^m	473 ^w	432
[Co(u)(his) (H_2O)Cl]	-	u-3320 ^{w,br} his-3037 ^{w,br}	u-3432 ^{br} his-3130 ^{w,br}	1637 ^w	1421 ^w	1628 ^m	u-1653 ^w his-1720 ^m	u-1474 ^w his-1075 ^m	1118 ^m	2757 ^w	1458 ^w	3037 ^{w,br}	2926 ^m	1272 ^w	1637 ^w	1534 ^w	2959 ^m	475 ^w	417 ^w
histidine	3010 ^w	-	-	1633 ^s	1414 ^s	1598	1734 ^m	1085 ^s	1111 ^s	2874 ^{br}	1460 ^s	3010 ^w	2925 ^w	1270 ^s	1633 ^s	1568 ^m	2968 ^w	-	-
urea	-	3353 ^m	3466 ^m	1618 ^{br}	-	-	1695 ^w	1468 ^{br}	-	-	-	-	-	-	-	-	-	-	-

s = strong, m = medium, br = broad, w = weak, w,br = weak and broad, b =bending

Magnetic and Electronic Spectral Studies

The electronic spectra of Cobalt (II), Nickel (II) and Copper (II) complexes as well as their magnetic moments have provided good evidence for the various structures of these complexes as shown in Table 4. The existence of a broad band at 20833 cm⁻¹ in the [Co(u)(his)(H₂O)]Cl electronic spectrum (Figure 4) may suggest a square-planar geometry (Structure 3). Also, the existence of the three bands at 13333, 14663 and 15576 cm⁻¹ confirms the proposed structure [25-27]. These observations together with the magnetic moment value (2.6 B.M.) support the presence of a square-planar environment around the Cobalt (II) ion [26,28]. Also, the dark brown color of the complex is in good agreement with those reported for square-planar Co^{II} complexes [26].

The complex [Ni(u)(his)(H₂O)₂]Cl has a magnetic moment of 2.9 B.M, which lies in the range reported for an octahedral geometry around the Ni^{II} ion with a ³A_{2g} ground term [23]. In addition, the complex has three bands in the UV-vis spectra recorded in DMSO solution (Figure 5); 21739cm⁻¹ may be attributed to the ³A_{2g}→³T_{1g} (v₃) and 16000 cm⁻¹ due to ³A_{2g}→³T_{1g} (v₂), while v₁ lies in the range of 13333cm⁻¹ transitions in an octahedral structure around the Ni^{II} ion (Structure 4) [23,28-30]. The green color of this complex is an additional evidence for octahedral structure [32,33].

The majority of Cu^{II} complexes are tetragonally distorted with four short metal-ligand bonds in one plane (xy) and two long metal-ligand bonds lying along the z-axis above and below this plane. The electronic spectrum of [Cu(u)(his)(H₂O)₃]Cl (Structure 5) in DMSO solution (Figure 6) shows strong band at 14577cm⁻¹. This band is due to ²E_g → ²T_{2g} transition, on the basis of which a distorted octahedral geometry is suggested [26,33,34]. The broadness of the observed band may be due to Jahn-Teller effect [34], which enhances the distortion of the octahedral geometry. The blue color of this complex supports the proposed geometry [33]. The magnetic moment value of this complex (1.62 B.M.) was found to be within

the range reported for the d⁹-system containing one unpaired electron [33,35].

Furthermore, previous studies proved that the broad bands centered at 24038 cm⁻¹, 23923 cm⁻¹ and 22026 cm⁻¹ should be assigned to charge-transfer transitions, for [Co(u)(his)(H₂O)]Cl [23], [Ni(u)(his)(H₂O)₂]Cl [36] and [Cu(u)(his)(H₂O)₃]Cl, respectively [31,36].

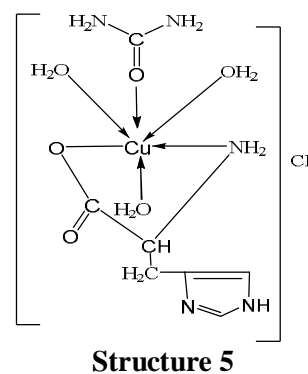
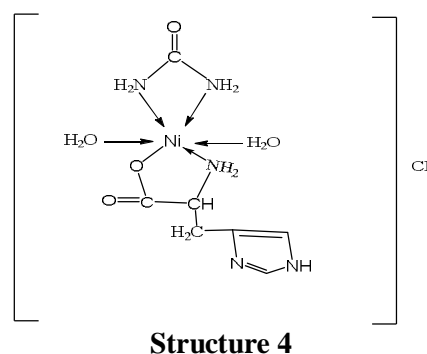
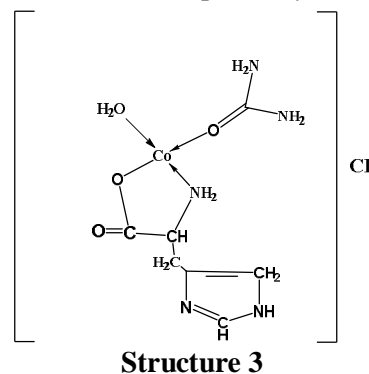


Table 4. Magnetic moment and electronic spectral data in DMSO solution for the complexes

Complex	μ_{eff} (B.M.)	Charge transfer bands (cm ⁻¹)	d-d transition bands (cm ⁻¹)	Supposed structure
[Co(u)(his)(H ₂ O)]Cl	2.6	24038	20833, 15576, 14663, 13333	Square-planar
[Ni(u)(his)(H ₂ O) ₂]Cl	2.9	23923	21739, 16000, 13333	Octahedral
[Cu(u)(his)(H ₂ O) ₃]Cl	1.62	22026	14577	Distorted octahedral

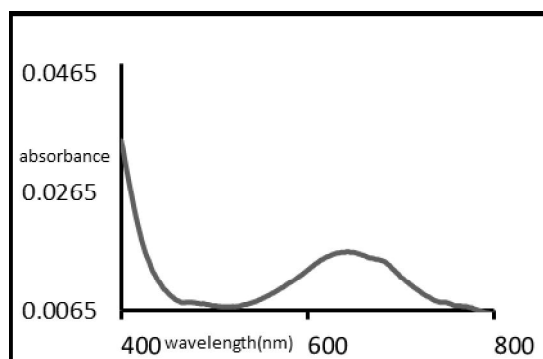


Figure 4. UV-visible electronic spectrum of $[\text{Co}(\text{u})(\text{his})(\text{H}_2\text{O})]\text{Cl}$ in DMSO solution.

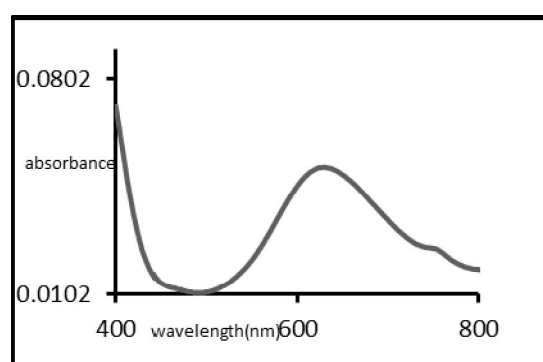


Figure 5. UV-visible electronic spectrum of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ in DMSO solution

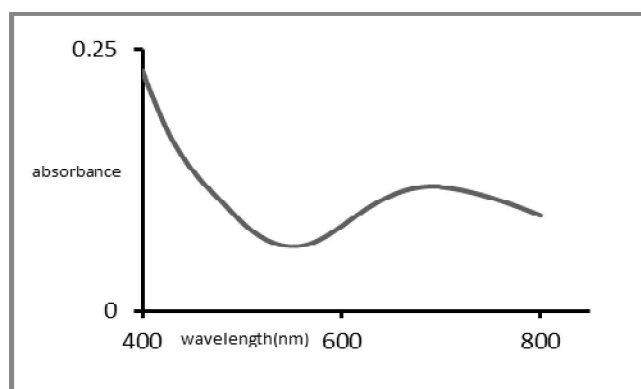


Figure 6. UV-visible electronic spectrum of $[\text{Cu}(\text{u})(\text{his})(\text{H}_2\text{O})_3]\text{Cl}$ in DMSO solution

Thermal Analysis of Ni-Urea-Histidine Complex

The TG degradation curves of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ in Figures 7 and 8 and the thermal parameters in Tables 5 and 6 reveal four decomposition stages at 22-179, 179-282, 282-404 and 404-546°C. The elimination of 100% coordinated water molecules with 13% Cl atoms exothermically occurs in the first step (cal. 11.8%, found 11.78%), exhibiting overlapping T_{DTG} and T_{dta} at 52°C and 68°C, respectively, with an activation energy of 86 $\text{kJ}\cdot\text{mol}^{-1}$ and 0.1

order reaction. The elimination of 70% Cl atoms exothermically occurs in the second step (cal. 7.21%, found 7.25%). The removal of remaining Cl atoms with 75% urea (cal. 14.83%, found 14.84%) takes place in the third step with T_{DTG} at 389°C and T_{dta} at 388°C. The fourth step suggests the slow bleed of remaining urea molecules and 56.97% histidine molecules (cal 29.86%, found 29.87%) as the T_{DTG} (528°C) and exothermic T_{dta} (516°C) peaks indicate. This step is of 1.1 order with an activation energy of 124 $\text{kJ}\cdot\text{mol}^{-1}$. The ill-defined residue at the end of the decomposition reaction is NiO and 4.19C (cal.

36.33%, found 36.33%). ΔS^* , ΔH^* and ΔG^* calculated are (-48.7, -124.4, -120.3 and -88.3.1 $\text{JK}^{-1}\text{mol}^{-1}$), (85.6, 100.3, 132.8 and 119.6 kJ mol^{-1}) and (88.1, 130.2, 179.6 and 166.2 kJ mol^{-1}), respectively.

Table 5. Characteristic parameters of thermal decomposition ($10^\circ\text{C min}^{-1}$) for $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ complex

Comp.	Step	TGA			DTA			Reaction
		$\Delta m\%$ found (calc.)	$T_i/^\circ\text{C}$	$T_f/^\circ\text{C}$	T_{DTG}	T_{dta}	Heat	
$[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$	1	11.78 (11.8)	22	179	52	68	endo	-[100% H_2O +13% Cl]
	2	7.25 (7.21)	179	282	243	246	endo	-[70% Cl]
	3	14.84 (14.83)	282	404	389	388	endo	-[17% Cl +75% urea]
	4	29.87 (29.86)	404	546	528	516	exo	-[25%urea +56.97%his.]
Final residue $\text{NiO}+4.19\text{C}$ (O=10.38%his, C=32.65%his): 36.33% (36.33%)								

Table 6. Kinetic and thermodynamic parameters of the thermal decomposition of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ complex

Comp.	Step	r	n	Z s^{-1}	T_{max} K	E_a kJ.mol^{-1}	ΔS^* $\text{J.K}^{-1}\text{mol}^{-1}$	ΔH^* kJ.mol^{-1}	ΔG^* kJ.mol^{-1}
$[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$	1	0.9921	0.1	3.1×10^9	52	86	-48.7	85.6	88.1
	2	0.9778	2.7	1.6×10^6	243	102	-124.4	100	130.2
	3	0.9973	4.9	4.2×10^6	389	136	-120.3	132.8	179.6
	4	0.9818	1.1	2.7×10^8	528	124	-88.3	119.6	166.2

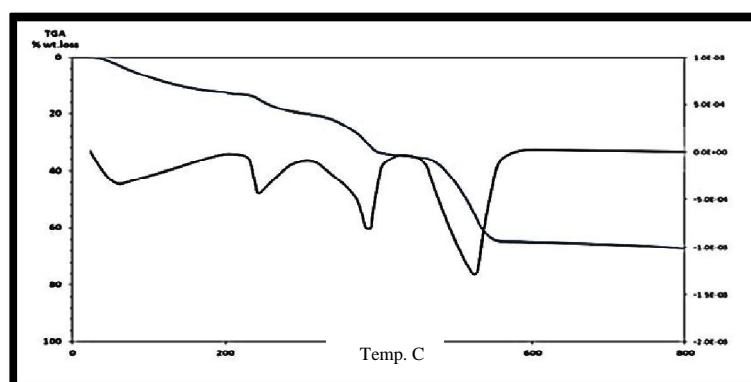


Figure 7. TG and DTG thermograms of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ complex.

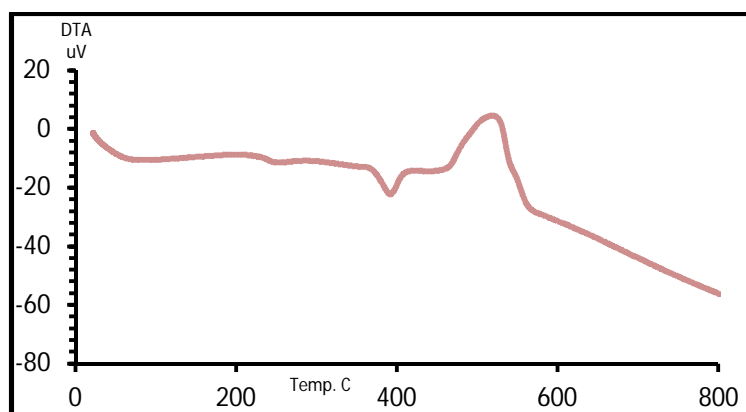


Figure 8. DTA thermogram of $[\text{Ni}(\text{u})(\text{his})(\text{H}_2\text{O})_2]\text{Cl}$ complex

Thermal Analysis of Cu-Urea-Histidine Complex

The thermolysis of $[\text{Cu}(\text{u})(\text{his})(\text{H}_2\text{O})_3]\text{Cl}$ in Figures 9 and 10 and the parameters in Tables 7 and 8 involve five successive steps at 24-125, 125-196, 196-276, 276-384 and 384-595 °C. The first step represents the elimination of 58.33% of coordinated water, (cal. 8.59%, found 8.58%) with an activation energy of 78 $\text{kJ}\cdot\text{mol}^{-1}$ and T_{DTG} at 75°C. The second step which is due to the release of 33.33% of coordinated water (cal. 4.91%, found 4.89%) has an activation energy of 96 $\text{kJ}\cdot\text{mol}^{-1}$ with a peak of T_{DTG} at 189°C and an exothermic peak of T_{dta} at 192°C. The third step of T_{DTG} at 242°C is assumed to correspond to a very slow elimination of remaining coordinated water and 80% of Cl atoms (cal. 8.95%, found 8.95%) with an

activation energy and a reaction order of 126 $\text{kJ}\cdot\text{mol}^{-1}$ and 0.9, respectively, with an exothermic peak of T_{dta} at 244°C. Elimination of remaining Cl atoms and 42.86% urea molecule (cal. 8.94%, found 8.97%) occurs in the fourth step of T_{DTG} at 355°C, which the final step (fifth) is assumed to correspond to the elimination of the remaining urea molecules and 89.62% of the histidine molecules (cal. 46.97%, found 47.95%), with an activation energy and a reaction order of 137 $\text{kJ}\cdot\text{mol}^{-1}$ and 0.9, respectively. There is a T_{DTG} peak at 554°C in the final step of the decomposition. The values (-142.2, -133.5, -168.6, -85 and 67.1 $\text{JK}^{-1}\cdot\text{mol}^{-1}$), (77.4, 94.4, 124, 116 and 132.4 $\text{kJ}\cdot\text{mol}^{-1}$) and (88.1, 119.6, 156.8, 146.2 and 169.6 $\text{kJ}\cdot\text{mol}^{-1}$) are their entropy, enthalpy and free energy changes of activation, respectively.

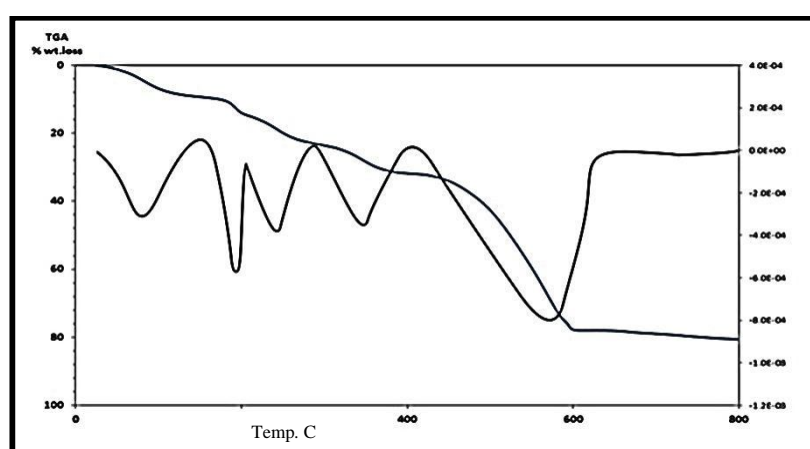
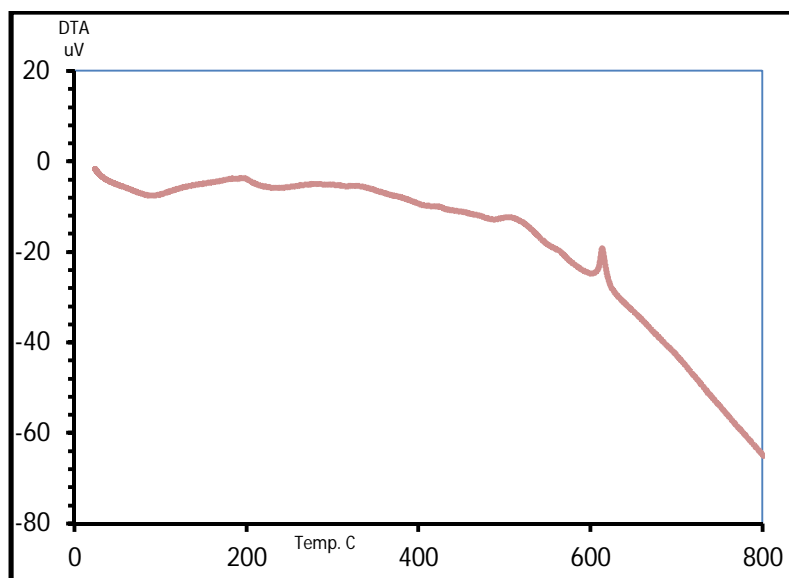
Table 7. Characteristic parameters of thermal decomposition ($10^\circ\text{C}\cdot\text{min}^{-1}$) for $[\text{Cu}(\text{u})(\text{his})(\text{H}_2\text{O})_3]\text{Cl}$ complex

Comp.	Step	TGA			DTA			Reaction
		$\Delta m\%$ found (calc.)	$T_i/^\circ\text{C}$	$T_f/^\circ\text{C}$	T_{DTG}	T_{dta}	Heat	
$[\text{Cu}(\text{u})(\text{his})(\text{H}_2\text{O})_3]\text{Cl}$	1	8.58 (8.59)	24	125	75	82	endo	-[58.33% H_2O]
	2	4.89 (4.91)	125	196	189	192	exo	-[33.33% H_2O]
	3	8.95 (8.95)	196	276	242	244	endo	-[8.34% H_2O + % 80Cl]
	4	8.97 (8.94)	276	384	355	329	exo	-[20% Cl+42.86 % U]
	5	46.95 (46.97)	384	595	554	570	exo	-[57.14% U+ 89.62% his.]

Final residue CuO (O=10.38%his): 21.66% (21.64%)

Table 8. Kinetic and thermodynamic parameters of thermal decomposition for [Cu(u)(his)(H₂O)₃]Cl complex

Comp.	Step	r	n	Z s ⁻¹	T _{max} K	E _a kJ.mol ⁻¹	ΔS* J.K ⁻¹ .mol ⁻¹	ΔH* kJ.mol ⁻¹	ΔG* kJ.mol ⁻¹
[Cu(u)(his)(H ₂ O) ₃]Cl	1	0.9994	5	5.8x10 ⁴	75	78	-142.2	77.4	88.1
	2	0.9952	4.8	4.2x10 ⁵	189	96	-133.5	94.4	119.6
	3	0.9965	0.9	7.9x10 ³	242	126	-168.6	124	156.8
	4	0.9789	2.5	2.7x10 ⁸	355	119	-85	116	146.2
	5	0.9903	0.9	3.6x10 ⁹	554	137	-67.1	132.4	169.6

**Figure 9. TG and DTG thermograms of [Cu(u)(his)(H₂O)₃]Cl complex****Figure 10. DTA thermogram of [Cu(u)(his)(H₂O)₃]Cl complex**

Antibacterial Activity of the Ligands and Their Complexes Formed

No inhibition zone was observed for the ligand histidine and formed complexes against the four studied strains (*Staphylococcus aureus*,

Bacillus subtilis, *Escherichia coli* and *Pseudomonas aeruginosa*), but free urea showed activity against *Bacillus subtilis* and *Escherichia coli* with inhibitory zones of 12mm and 10mm, respectively.

Table 9. Effect of the ligands and their complexes on the growth of bacteria (zone of inhibition in mm)

Compound (1000 $\mu\text{g/ml}$)	Bacteria			
	Gram-positive		Gram-negative	
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Pseudomonas aeruginosa</i>	<i>Escherichia coli</i>
urea	-	++	-	-
histidine	-	-	-	-
[Co(u)(his)(H ₂ O)]Cl Cl	-	-	-	-
[Ni(u)(his)(H ₂ O) ₂]Cl	-	-	-	-
[Cu(u)(his)(H ₂ O) ₃]Cl	-	-	-	-
Gentamicin 120 $\mu\text{g/ml}$	++	+	++	+

(-) No zone of inhibition was observed.

Moderately sensitive, (+) inhibition zone of 2-5mm.

Sensitive, (++) inhibition zone of 6-10mm.

Highly sensitive, (+++) inhibition zone of 11-15mm.

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