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Synthesis, characterization and comparative thermal degradation study of Co(II), Ni(II) and Cu(II) complexes with Asparagine and Urea as mixed ligands

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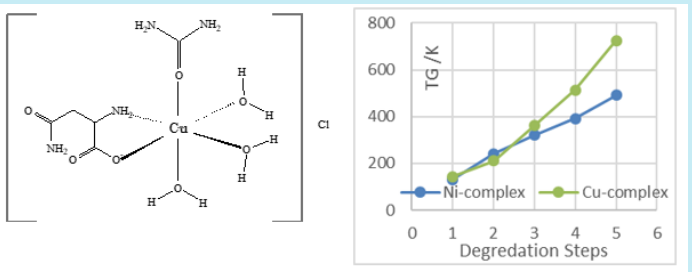
ABSTRACT: New Co(II), Ni(II) and Cu(II) complexes with urea and asparagine as ligands have been synthesized in (M:L_1:L_2) molar ratio (where M= Co(II), Ni(II) and Cu(II), L_1 = urea, and L_2 = asparagine) then identified by micro analyses, molar conductance measurements, IR, ^{1}HNMR, Mass, UV-VIS spectroscopies and magnetic susceptibility measurements. Thermal degradation studies were carried out by thermal analysis. These complexes have the general formula $[M(L_1)(L_2)(H_2O)_n]Cl$. The molar conductance values in DMSO solvent show the electrolytic nature of these complexes, indicating the outer-sphere coordination of the chloride anions with metal ions. The three complexes have an octahedral structure with urea molecule showing two modes of coordination. Thermal analysis study shows the rapid decomposition reaction for Ni complex and the highest thermal stability for Cu complex. The kinetic parameters were determined from the thermal decomposition data using the Coats-Redfern method. Thermodynamic parameters were calculated using standard relations.



New complexes of urea and asparagine coordinated to M (Co^{2+}, Ni^{2+} and Cu^{2+}) were prepared and an octahedral structure was proposed. Cu complex presented higher thermal stability.

1. Introduction

Recently, there has been renewed attention in the preparation and studies of mixed ligand transition metal complexes[1, 2] due to their new useful properties such as magnetic exchange, photoluminescence, nonlinear optical property, electrical conductivity and antimicrobial activity[3-5].

Mixed ligand complexes containing amino acid as co-ligand are potential biomimetic models for metal-protein interaction[6]. Research has shown significant progress in utilization of transition metal complexes as drugs to treat a lot of human diseases like carcinomas, infection control, anti-inflammatory, diabetes and neurological disorders[7].

Urea, carbamide or carbonyldiamide $CO(NH_2)_2$ (Figure 1a), which has a remarkable role in many biological processes in decomposition of proteins and amino acid catabolism, was discovered in 1828 by Wöhler when evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate[8].

The mode of urea bonding with metal ions seems to be dependent upon the type and nature of the metal, lead(II) coordinates to the nitrogen atom, whereas iron(III), zinc(II) and copper(II)

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coordinate to the oxygen of urea[9]. Also, there are different types of coordination of urea in its complexes with rare-earth iodides and perchlorates[10].

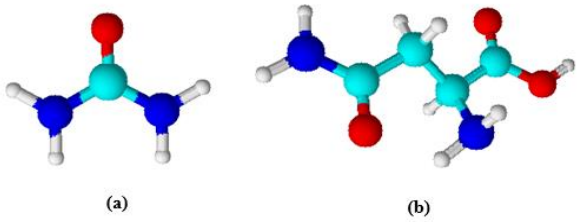

Figure 1. Structures of urea (a) and asparagine (b) molecules.

The amino acids are the main building units of all various forms of life and were earlier discovered as ingredient of natural products even before they were recognized as components of proteins[11]. The amino acid L-asparagine or 2-amino-3-carbamoylpropanoic acid (Fig. 1b) is a structural analog of L-aspartic acid. It was the first amino acid to be isolated from plants 200 years ago and because it has an N:C ratio of 2:4, this makes it an efficient molecule for the storage and transport of nitrogen in living organisms[12]. There are some similar thermal studies of various types of mixed ligands with transition metals[1, 2, 13-15], however, no previous studies on the synthesis, characterization and thermal studies of the mixed ligand complexes of urea and asparagine acid have been reported. Hence, the present work reports the preparation, characterization and thermal study of new mixed ligand complexes of urea and asparagine with Co(II), Ni(II) and Cu(II) ions.

2. Materials and methods

2.1 Chemicals

All chemicals such as solvents, metal(II) chlorides (i.e. $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CoCl_2.2H_2O$) were commercially available from BDH and were used without further purification.

2.2 Instrumentation

The melting points of the metal complexes were measured in glass capillary tubes with a Stuart Scientific Electrothermal melting point apparatus. TLC was carried out on silica gel GF_{254} plates (mn-kieselgel G., 0.2 mm thickness) with a 3:1 v/v ethyl acetate / petroleum ether solution as eluent mobile at room temperature. The plates were scanned under ultraviolet light lamp of 254 nm. The CHN elemental analysis of the complexes was carried out by Vario ELFab. Chloride was determined volumetrically by silver nitrate. The amount of H_2O was determined gravimetrically using weight loss method. Perkin-Elmer 2380 flame atomic absorption spectrophotometer was used for the determination of metal content. Jenway conductivity meter model 4510 was used for measuring the molar conductance of the freshly prepared metal complexes solutions (10^{-3} mol L^{-1} in DMSO) at room temperature. IR spectra of the metal complexes were measured in the range 200-4000 cm^{-1} with a FT/IR–140 (Jasco, Japan). Varian FT-300 MHz spectrometer was used for recording ^{1}HNMR spectra in d_6DMSO solvent and TMS as internal standard. Mass spectra were recorded in a Jeol JMS600 spectrometer. The electronic spectra of the complexes were measured in the range 400–800 nm, using UV–VIS spectrophotometer Specord 200, Analytilk Jena (Germany). The magnetic susceptibility of the solid complexes was measured at room temperature using Gouy's method by a balance from Johnson Metthey and Sherwood model. The Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) experiments were performed under nitrogen atmosphere using a platinum sample pan at a flow rate of 30 mL min^{-1} and a 10 °C min^{-1} heating rate for the temperature range 25–800 °C in Shimadzu DTA-50 and Shimadzu TGA-50H thermal analyzers, respectively, at Micro Analytical Center, Cairo University, Egypt.

2.3 Synthesis of mixed ligand complexes

Generally, the solid complexes were prepared by adding dropwise an ethanolic solution of hydrated metal(II) chlorides (0.01 mol) to an ethanolic solution of urea (0.01 mol) with stirring. The mixture was refluxed for 12 h with persistent stirring. A hot solution of 0.01 mol asparagine in 1:1 ethanol / water mixture ratio with drops of 1 mol L^{-1} NaOH was used to adjust the pH at 7-7.5 and to deprotonate NH_3^+ in the asparagine to NH_2. The mixture was refluxed for 2 h until the formation of colored precipitate occurred. All the solutions were in 1:1:1 molar ratio. The end products were filtered off and washed with distilled water to remove NaCl, followed by absolute ethanol until the solution became clear, and after

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that the product was washed with DMF and left to dry[16]. The yield was 56%, 52% and 42% for Co, Ni and Cu-complexes, respectively.

3. Results and discussion

Complexes of Co(II), Ni(II) and Cu(II) with urea and asparagine are studied. Some physical properties, molar conductivity and analytical data are summarized in Tables 1 and 2. The elemental analysis proves that the complexes of Co(II), Ni(II) and Cu(II) with urea (ur) and asparagine (A_{asn}) ligands are of 1:1:1 (metal:ur:asn) molar ratio. The molar conductivity values indicate that the chloride anions are in the outer-sphere of these complexes.

Table 1. Some properties of the complexes.

Complex proposed formula	Color	M.p / °C	TLC		Molar conductivity Λ_m/S cm^2 mol^{-1}
			No. of spots	R_f	
[Co(ur)(asn)(H_2O)$_2$]Cl [Co($C_5H_{15}N_4O_6$)]Cl	dark violet	203±1	One	0.18	133
[Ni(ur)(asn)(H_2O)$_2$]Cl [Ni($C_5H_{15}N_4O_6$)]Cl	bluish green	185±1	One	0.24	128
[Cu(ur)(asn)(H_2O)$_3$]Cl [Cu($C_5H_{17}N_4O_7$)]Cl	light violet	337±1	One	0.32	140

Table 2. The elemental analysis of the complexes.

Complex proposed formula	Molecular weight		Elemental analysis									
			%C		%H		%N		%M		%Cl	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
[Co(ur)(asn)(H_2O)$_2$]Cl [Co($C_5H_{15}N_4O_6$)]Cl	321.58	321.61	18.67	18.67	4.70	4.70	17.42	17.42	18.33	18.32	11.03	11.04
[Ni(ur)(asn)(H_2O)$_2$]Cl [Ni($C_5H_{15}N_4O_6$)]Cl	321.34	321.36	18.68	18.69	4.70	4.71	17.44	17.44	18.27	18.26	11.03	11.05
[Cu(ur)(asn)(H_2O)$_3$]Cl [Cu($C_5H_{17}N_4O_7$)]Cl	344.21	344.23	17.44	17.45	4.98	4.89	16.28	16.28	18.46	18.46	10.29	10.31

3.1 IR Spectra of urea-asparagine complexes

In these complexes, urea acts in two ways: as a monodentate ligand through oxygen of C=O, or as a bidentate through nitrogen of two NH_2 groups, while asparagine acts as an anion bidentate molecule, through COO^- group and NH_2 group. The assignment of the distinctive bands is summarized in Table 3 and the IR spectra of complexes are shown in Figures 2 to 4.

The IR spectra of the complexes show additional broad bands in the range 3386-3430 cm^{-1} due to the υ(OH) stretching of water molecule. Coordinated water is also identified by the appearance of ρ_r (rocking) and ρ_w (wagging) approximately at 875 cm^{-1} and 521 cm^{-1}, respectively. These results agree with the elemental analysis and thermogravimetric studies[17]. The υ(NH_2) stretching vibrations of free urea at υ_s3353 cm^{-1} and υ_{as}3466 cm^{-1} were shifted to lower wave numbers in the spectra of the complexes of Co(II) and Ni(II). This fact shows that the υ(NH_2) group must be involved in coordination while υ(CO) shifted to higher frequency[18].

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Table 3. Main IR bands (cm^{-1}) of the urea-asparagine complexes.

Urea	Asparagine	$[Co(ur)(asn)(H_2O)_2]Cl$	$[Ni(ur)(asn)(H_2O)_2]Cl$	$[Cu(ur)(asn)(H_2O)_3]Cl$	Assignment
-	3110m	-	-	-	$\upsilon(NH_3^+)$
3353m	3182m	ur-3320w asn-3185w,br asn-3227br	ur-3250 asn-3179br asn-3235br	ur-3298 m asn-3189br asn-3265 m	$\upsilon_S(NH_2)$
3466 m	3182m	ur-3420br asn-3185w,br asn-3320w,br	ur-3430br asn-3179br asn-3235br	ur-3337m asn-3189br asn- 3386m	$\upsilon_{as}(NH_2)$ H_2O, $\upsilon(OH)$
1618br	1644m	1637w	1637w	1629m	$\delta(NH)$
-	1428s	1412 s	1420w	1423w	$\upsilon_s(COO^-)$
-		1509 w	1509 w	1509w	$\upsilon_{as}(COO^-)$
1695w	1745w 1681m	ur-1719w asn-1773w asn-1662m	ur-1725 s asn-1773w asn-1655m	ur-1629m asn-1773w asn- 1665m	$\upsilon(CO)$
1468br	υ(C-N)1074s υ(O=C-N)1399m	ur-1446w asn-1081m asn-1409w,br	ur-1459m asn-1040 m asn-1410 w	ur-1490w asn-1039w asn1413m-	υ(C-N)
-	2874w	2873 w	2858 m	2857w	$\upsilon(CH_2)$
-	1428s	1445w	1420w	1439w	$\delta(CH_2)$
-		472 w	476w	454m	υ(M-O)
-		422w	421w	413m	υ(M-N)

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

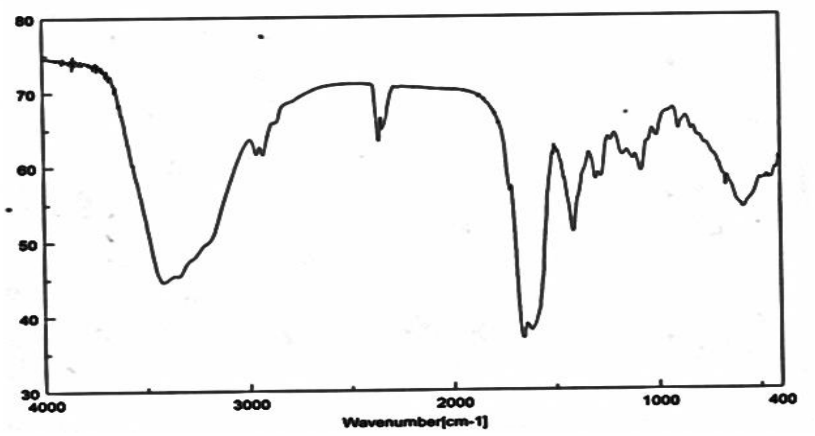

Figure 2. IR spectrum of $[Co(ur)(asn)(H_2O)_2]Cl$.

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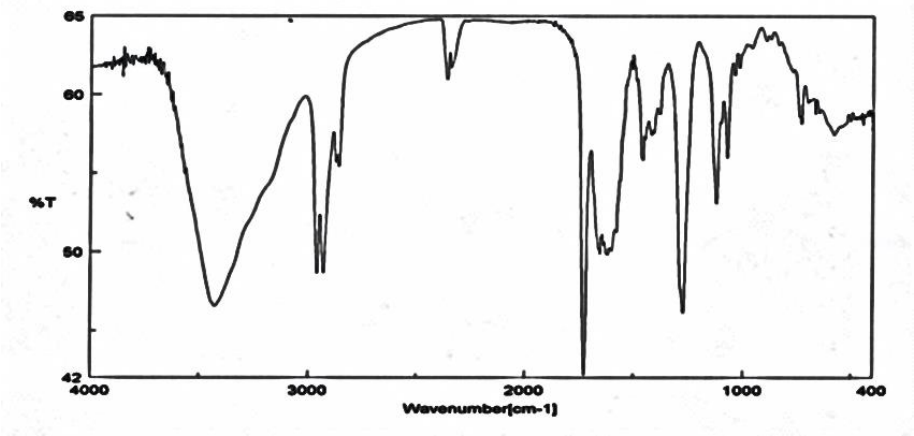

Figure 3. IR spectrum of [Ni(ur)(asn)$(H_2O)_2$]Cl.

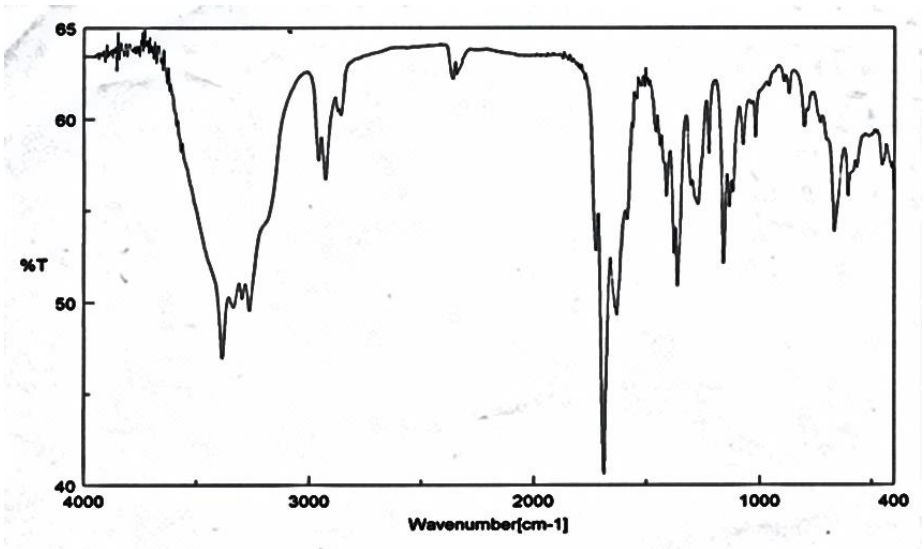

Figure 4. IR spectrum of [Cu(ur)(asn)$(H_2O)_3$]Cl.

The IR spectrum of the Cu(II)-complex showed a new band at 1629 cm^{-1} assigned to υ(C=O-Cu(II)) with slight change in υ(NH_2) vibration[19]. In comparison with asparagine, $\upsilon_s(COO^-)$ and $\upsilon_{as}(COO^-)$ shift to lower wave numbers, confirming the monodentate nature of the coordinated carboxylate group[20].

The υ(NH_3^+) band at 3110 cm^{-1}, which is specific for the zwitterion in asparagine, vanished in the spectra of the complexes after the deprotonation of NH_3^+ to NH_2. Therefore, the higher wave numbers shift of the bands assigned to $\upsilon_{as}(NH_2)$ and $\upsilon_s(NH_2)$ indicates that the NH_2 group is imminently involved in the coordination[20].

IR of the prepared complexes showed weak bands in the range of 476-454 cm^{-1} and 422-413 cm^{-1}, attributed to υ(M-O) and υ(M-N), respectively[21]. Other bands are listed in Table 3.

3.2 ^{1}HNMR spectra of urea-asparagine complexes

^{1}HNMR spectra of [Co(ur)(asn)$(H_2O)_2$]Cl, [Ni(ur)(asn)$(H_2O)_2$]Cl and [Cu(ur)(asn)$(H_2O)_3$]Cl complexes show various signals which were summarized in Table 4. Urea shows a new signal at 5 and 5.1 ppm in Co(II) and Ni(II) complexes, respectively, for the amide groups coordinated to the metal atom without proton displacement[22], while in Cu(II) complex only carbonyl group is coordinated to metal[22]. The signals at 3.2, 3.1 and 2.85 ppm are assigned to CH group, whereas signals at 2.9, 2.45 and 2.5 ppm of CH_2 group are observed for Co(II), Ni(II) and Cu(II) complexes, respectively. The appearance of a new signal around 2.6-2.7 ppm is attributed to NH_2 group of asparagine and the amide group shows signals in the range 6.3-6.7 ppm[23]. The coordinated H_2O shows a new signal around 3.5-3.7 ppm[24].

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Table 4. [1]HNMR chemical shift of free urea and asparagine ligands and their complexes.

System	$(CH)_{\alpha}$	$(CH)_{\beta}$	NH_3^+	$NH_{2(asn)}$	$NH_{2(ur)}$	H_2O
Urea	-	-	-	-	6-7.5	-
Asparagine	4.6	2.6	7-8	6.9-7.6	-	-
$[Co(ur)(asn)(H_2O)_2]Cl$	3.2	2.9	-	6.6, 2.7	$5_{(bonding)}$	3.7
$[Ni(ur)(asn)(H_2O)_2]Cl$	3.1	2.45	-	6.3, 2.7	$5.1_{(bonding)}$	3.55
$[Cu(ur)(asn)(H_2O)_3]Cl$	2.85	2.5	-	6.7. 2.6	$6.4_{(nonbonding)}$	3.5

3.3 Mass spectra of urea – asparagine complexes

The mass spectra of Co(II), Ni(II) and Cu(II) complexes with urea and asparagine ligands exhibited the molecular ion peaks at m/z (calc. 321.58, found 321.61; calc. 321.34, found 321.36 and calc. 344.21, found 344.23), respectively.

The molecular ion of $[Co(ur)(asn)(H_2O)_2]Cl$ complex loses NH_4Cl and $H_2NCH_2COO^-$ leaving ions at m/z 268.13 and 247.07, respectively; then loses NH_2 and H_2O fragments, giving an ion at m/z 212.08. The spectrum of $[Ni(ur)(asn)(H_2O)_2]Cl$ complex shows a peak at m/z 267.89, indicating the loss of H_2O and $½Cl_2$. The molecule of $[Cu(ur)(asn)(H_2O)_3]Cl$ loses $H_2O + NH_2$ and $½Cl_2 + H_2O$, leaving ions at m/z 310.07 and 290.76, respectively. The ion at m/z 310.07 loses CO_2, leaving an ion at m/z 266.09, which further loses $½N_2$ to leave an ion at m/z 252.01. Afterwards, this last ion gives a new peak at m/z 234, indicating loss of H_2O and the remaining fragment loses another CO, leaving an ion at m/z 206.05.

3.4 Magnetic and electronic spectral studies

The electronic spectra of the Co(II), Ni(II) and Cu(II) complexes as well as their magnetic moment data have provided good evidence for the structures of these complexes as shown in Table 5. For $[Co(ur)(asn)(H_2O)_2]Cl$, hexa-coordination is suggested as in Figure 5a, based on the appearance of bands at 18248 cm^{-1} and at 14534 cm^{-1} (Figure 6), which were attributed to the $^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (υ_3) and $^4T_{1g} \rightarrow {}^4A_{2g}$ (υ_2) transitions, respectively[25]. The third band, υ_1, could not be observed due to the limited range of the instrument used (200-1100 nm). Also, the magnetic moment of 4.81 B.M is within the range reported for a high-spin octahedral geometry around the Co(II) ion[26].

Table 5. Magnetic moments 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}	Proposed structure
$[Co(ur)(asn)(H_2O)_2]Cl$	4.81	23585	18248, 14534	Octahedral
$[Ni(ur)(asn)(H_2O)_2]Cl$	2.9	24510	22727, 16181, 14619	Octahedral
$[Cu(ur)(asn)(H_2O)_3]Cl$	1.84	22727	16026	Distorted octahedral

$[Ni(ur)(asn)(H_2O)_2]Cl$ complex has a magnetic moment of 2.9 B.M, which is within the range reported for an octahedral geometry around the Ni(II) ion with a $^3A_{2g}$ ground term[27]. In addition, this complex has three bands in the UV-VIS spectrum (Figure 7): the band at 22727 cm^{-1} may be attributed to $^3A_{2g} \rightarrow {}^3T_{1g}$ (υ_3); 16181 cm^{-1} due to $^3A_{2g} \rightarrow {}^3T_{1g}$ (υ_2) and υ_1 at 14619 cm^{-1} in accordance with an

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octahedral structure around the Ni(II) ion (Fig. 5a)[25, 28]. The electronic spectrum of [Cu(ur)(asn)$(H_2O)_3$]Cl (Fig. 5b and Fig. 8) shows a strong band at 16026 cm^{-1}. This band is due to $^2E_g \rightarrow {}^2T_{2g}$ transition and a distorted octahedral geometry is suggested[25]. The broadness of this band may be due to Jahn-Teller effect[25], which confirms the distorted octahedral geometry. The magnetic moment value (1.84 B.M) is also within the range reported for the d^9-system containing one unpaired electron[29]. The bands at 23585 cm^{-1}, 24510 cm^{-1} and 22727 cm^{-1} should be attributed to the charge transfer transitions in the complexes [Co(ur)(asn)$(H_2O)_2$]Cl, [Ni(ur)(asn)$(H_2O)_2$]Cl and [Cu(ur)(asn)$(H_2O)_3$]Cl, respectively[30].

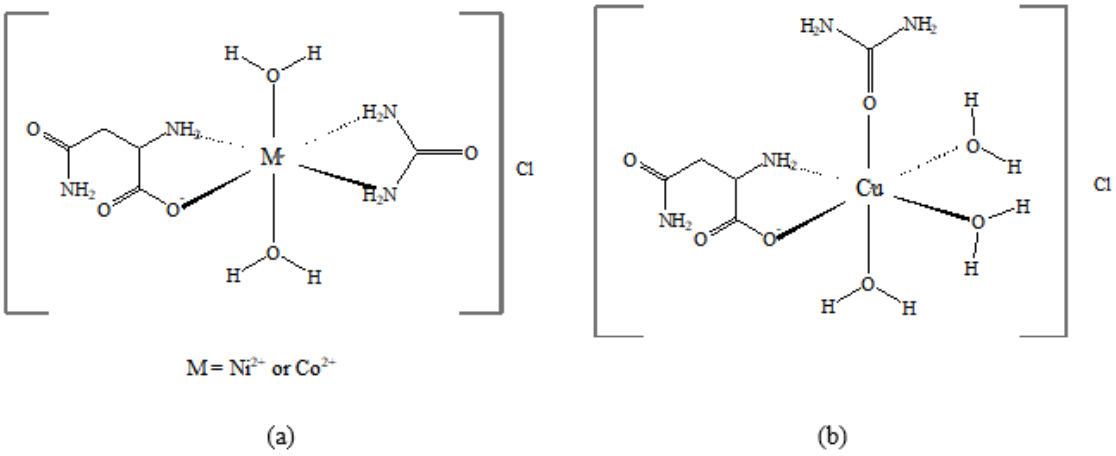

Figure 5. Suggested structure of the complexes.

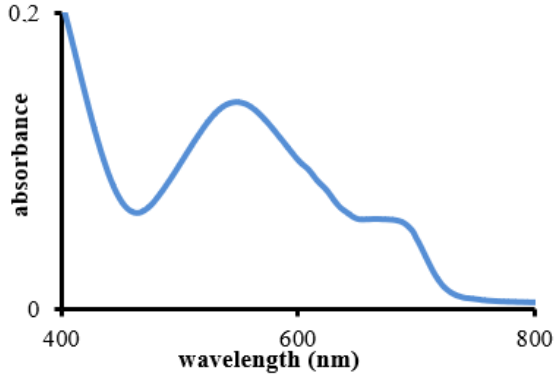

Figure 6. UV-VIS spectrum of [Co(ur)(asn)$(H_2O)_2$]Cl complex in DM.

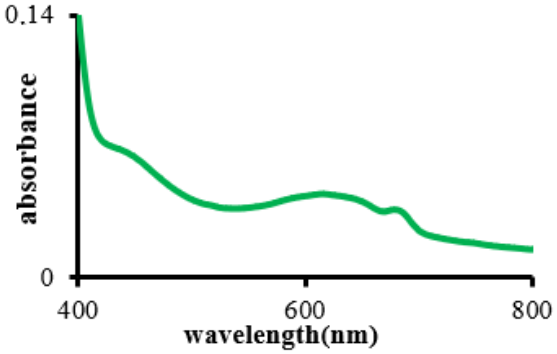

Figure 7. UV-VIS spectrum of [Ni(ur)(asn)$(H_2O)_2$]Cl complex in DMSO solution.

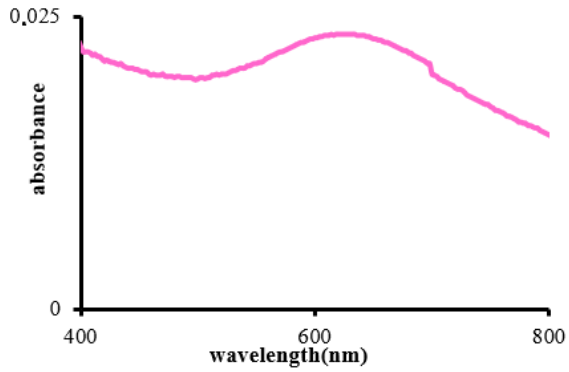

Figure 8. UV-VIS spectrum of [Cu(ur)(asn)$(H_2O)_3$]Cl complex in DMSO solution.

4.5 The Thermal degradation study

The TGA and DTA curves of the prepared Ni and Cu complexes are given in Figures 9 to 12. These curves characterize and compare the thermal degradation of these two complexes at 10 °C min^{-1} heating rate, under nitrogen and between 20-800 °C. For the evaluation of the thermal degradation kinetics parameters at a single heating rate (10 °C min^{-1}), the activation energy (E_a) and pre-exponential factor (Z) are determined by using the Coats-Redfen method for the reaction order $n \neq 1$. When the Coats-Redfern method is

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linearized for a correctly-chosen order of reaction (n) yields the activation energy (E_a) from the slope of the equation:

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

where: α = fraction of weight 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 (ΔH*), entropy (ΔS*), and Gibbs energy (ΔG*) of activation are calculated using the following standard equations:

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

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

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

The characteristics of the thermal degradation of these two complexes recorded on the TG/DTG/DTA curves, their kinetics and thermodynamics parameters extracted from these curves are given in Tables 6-9.

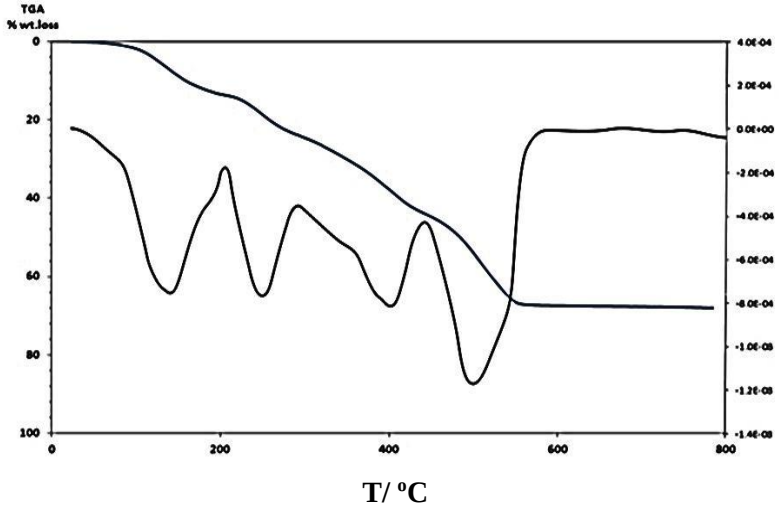

Figure 9. TG and DTG curves of [Ni(ur)(asn)$(H_2O)_2$]Cl complex.

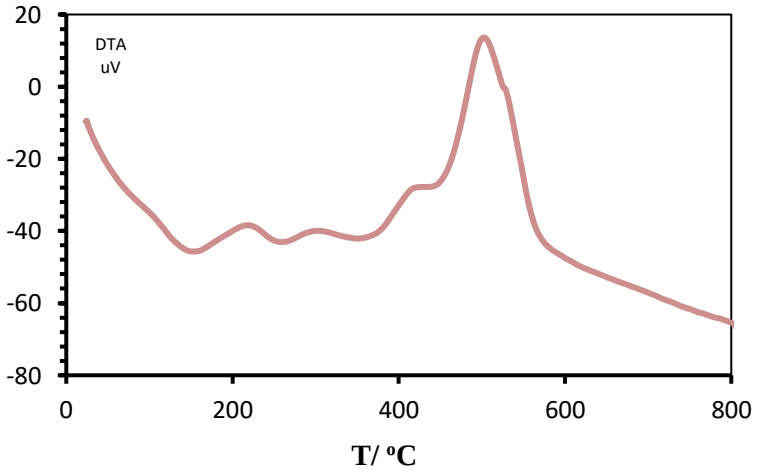

Figure 10. DTA curve of [Ni(ur)(asn)$(H_2O)_2$]Cl complex.

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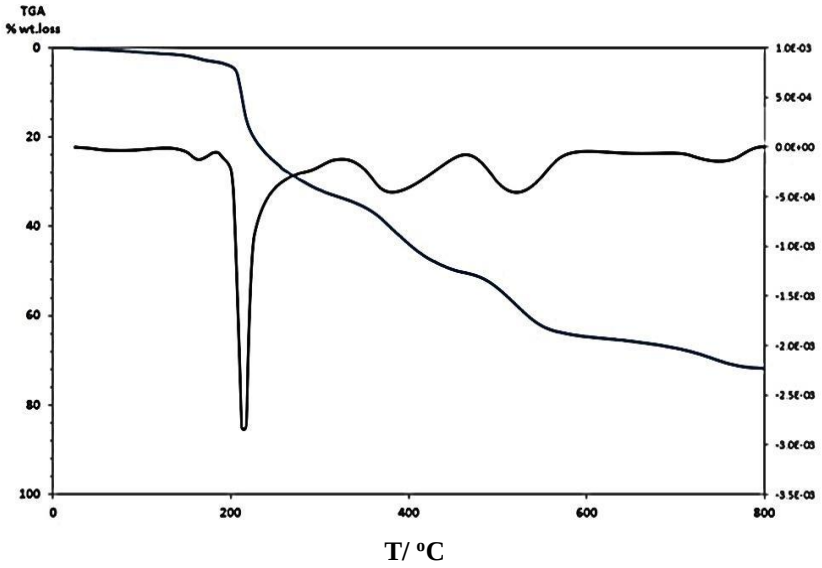

Figure 11. TG and DTG curves of [Cu(ur)(asn)$(H_2O)_3$]Cl complex.

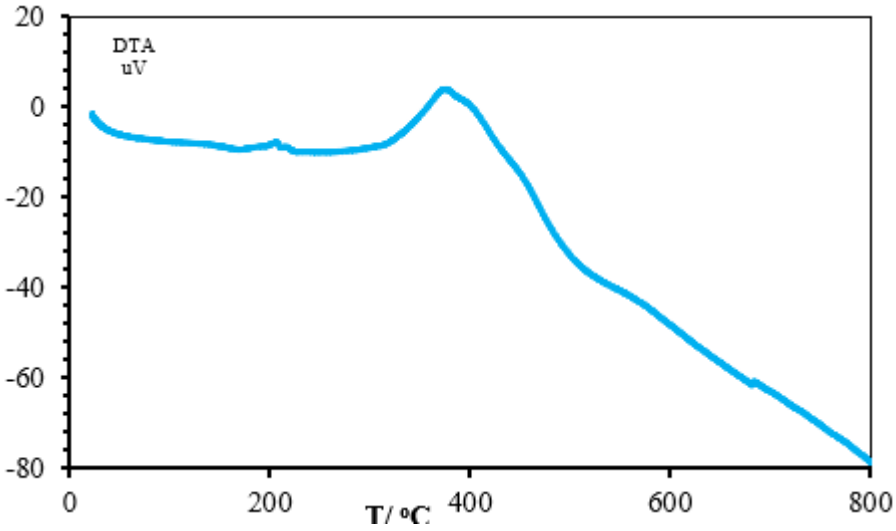

Figure 12. DTA curve of [Cu(ur)(asn)$(H_2O)_3$]Cl complex.

4.5.1 Thermal analysis of [Ni(ur)(asn)$(H_2O)_2$]Cl

The thermolysis of [Ni(ur)(asn)$(H_2O)_2$]Cl (Tables 6 and 7) and (Figures 9 and 10) involves several successive steps at 24-186, 186-274, 274-351, 351-428 and 428-552 °C. The first step represents the elimination of 100% coordinated H_2O molecules and 12.5% of a chloride atom (calc. 12.59%, found 12.58%) with activation energy E_a = 93 kJ mol^{-1} and a T_{DTG} peak at 132 °C. The second step corresponds to the loss of the remaining 87.5% Cl atom (calc. 12.12%, found 12.11%) which has E_a of 124 kJ mol^{-1} with T_{DTG} at 242 °C and exothermic peak T_{DTA} at 248 °C. According to the DTG curve (Figure 8), the third step is assigned to the removal of 42.86% urea molecule (calc. 8.01%, found 8.00%) and with E_a and reaction order (n) of 114 kJ mol^{-1} and 0.1, respectively. The fourth step which corresponds to the loss of the remaining urea molecule and 3.52% of asparagine (calc. 12.12%, found 12.11%) has E_a = 129 kJ mol^{-1}. The final step corresponds to the 59.82% loss of asparagine (calc. 24.41%, found 24.44%) with E_a = 131 kJ mol^{-1} and a T_{DTG} peak at 491 °C. The final residue is NiO and carbon (2.67%) as ash (O=12.2%asn, C=24.46%asn) (calc. 33.21%, found 33.21%). The values of ΔS*, ΔH* and ΔG* are: -12.4, -117.9, -165, -120.4 and -144.5 J K^{-1} mol^{-1}; 91.9, 122, 111.3, 125.7 and 126.9 kJ mol^{-1}; and 93.5, 150.5, 164.3, 172.8 and 197.8 kJ mol^{-1}, respectively, for the steps observed in the thermal decomposition of the complex.

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Table 6. Characteristic parameters of thermal decomposition (10 °C min^{-1}) for $[Ni(ur)(asn)(H_2O)_2]Cl$.

Comp.	Steps	TGA				DTA		mass loss
		Δm % found (calc.)	T_i/°C	T_f/°C	T_{DTG}	T_{DTA}	Heat	
[Ni(ur)(asn)(H2O)2]Cl	1	12.58 (12.59)	24	186	132	134	endo	-[100%H_2O+12.5% Cl]
	2	9.66 (9.66)	186	274	242	248	exo	-[87.5% Cl]
	3	8.00 (8.01)	274	351	321	321	exo	-[42.86% ur]
	4	12.11 (12.12)	351	428	391	408	exo	-[57.14% ur+3.52% asn]
	5	24.44 (24.41)	428	552	491	500	exo	[59.82% asn]
Final residue NiO +2.67C (O=12.2%asn, C=24.46%asn): 33.21% (33.21%)								

Table 7. Kinetic and thermodynamic parameters of the thermal decomposition of $[Ni(ur)(asn)(H_2O)_2]Cl$.

Comp.	Steps	r	*n*	Z / s^{-1}	T_{max} / K	E_a / kJ mol^{-1}	Δ*S** / J K^{-1} mol^{-1}	Δ*H** / kJ mol^{-1}	Δ*G** / kJ mol^{-1}
[Ni(ur)(asn)(H2O) 2]Cl	1	0.9794	2.6	$6.2x10^{11}$	132	93	-12.4	91.9	93.5
	2	0.9447	0.9	$3.5x10^{6}$	242	124	-117.9	122	150.5
	3	0.9998	0.1	$1.6x10^{4}$	321	114	-165	111.3	164.3
	4	0.9975	4.9	$4.2x10^{6}$	391	129	-120.4	125.7	172.8
	5	0.9974	2.8	$2.9x10^{5}$	491	131	-144.5	126.9	197.8

r = correlation coefficient of the linear plot, n = order of reaction, Z = pre-exponential factor.

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Table 8. Characteristic parameters of thermal decomposition (10 °C min^{-1}) for $[Cu(ur)(asn)(H_2O)_3]Cl$.

Comp.	Steps	TGA				DTA		mass loss
		Δm % found (calc.)	T_i/°C	T_f/°C	T_{DTG}	T_{DTA}	Heat	
$[Cu(ur)(asn)(H_2O)_3]Cl$	1	2.98 (2.99)	22	178	143	168	endo	-[19.05% H_2O]
	2	29.35 (29.35)	178	306	211	207	exo	-[80.95%H_2O+100%Cl + 36.36% ur]
	3	17.35 (17.37)	306	449	362	376	exo	-[63.64% ur+16.46% asn]
	4	16.44 (16.46)	449	666	514	-	-	-[43.20% asn]
	5	5.51 (5.49)	666	785	725	-	-	-[14.40% asn]
Final residue CuO + 1.5% C (O=12.2% asn, C=13.74% asn): 28.37% (28.34%)								

Table 9. Kinetic and thermodynamic parameters of the thermal decomposition of $[Cu(ur)(asn)(H_2O)_3]Cl$.

Comp.	Steps	r	*n*	Zvz / s^{-1}	T_{max} / K	E_a / kJ mol^{-1}	Δ*S** / J K^{-1} mol^{-1}	Δ*H** / kJ mol^{-1}	Δ*G** / kJ mol^{-1}
$[Cu\ (ur)(asn)(H_2O)_3]Cl$	1	0.9916	4.8	$2.4x10^8$	143	98	-192.6	96.8	124.3
	2	0.9689	5	$1.9x10^7$	211	119	-102.7	117.2	138.7
	3	0.9855	2.2	$3.8x10^8$	362	134	-82.3	135	165.2
	4	0.9946	3.5	$2.7x10^6$	514	123	-126.3	118.7	183.6
	5	0.9972	4.9	$3.2x10^5$	725	137	-146.9	134	240.5

r = correlation coefficient of the linear plot, *n* = order of reaction, *Z* = pre-exponential factor.

4.5.2 Thermal analysis of $[Cu(ur)(asn)(H_2O)_3]Cl$

The TG and DTG curves of $[Cu(ur)(asn)(H_2O)_3]Cl$ (Tables 8 and 9) and (Figures 11 and 12) show five steps of a continuous mass loss with DTG peaks indicating slow mass losses. The first step (22-178 °C) at T_{DTG} 143 °C is attributed to the release of 19.05% of coordinated H_2O (calc. 2.99%, found 2.98%). The remaining loss of H_2O, and the loss of 100% Cl and 36.36% of urea occur in the second step (178-306 °C). Third (306-449 °C), fourth (449-666 °C) and fifth (666-785 °C) steps are due to the release of [63.64%ur+16.46%asn], [43.20%asn] and [14.40%asn] fragments (calc. 17.37%, found 17.35%; calc. 16.46%, found 16.44% and calc. 5.49%, found 5.51%), respectively, at the T_{DTG} peaks at 362, 514 and 725 °C (Figure 9), respectively. The E_a calculated of these five steps are 98, 119, 134, 123 and 137 kJ mol^{-1}, respectively, and the values of ΔS*, ΔH* and ΔG* are: -192.6, -102.7, -82.3, -126.3 and -146.9 J K^{-1} mol^{-1}; 96.8, 117.2, 135.0, 118.7 and 134.0 kJ mol^{-1}, and 124.3, 138.7, 165.2, 183.6 and 240.5 kJ mol^{-1}, respectively, for the steps observed in the thermal decomposition of the complex.

4.5.2 General remarks of thermal degradation:

1. Thermal analysis confirms the presence of coordinated water molecules.

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2. Sharp peak in Ni-complex means that the leaving parts move away faster than that in Cu-complex.
3. The releasing of the urea ligand before asparagine ligand may be due to non-ionic bonding of this ligand with the metal ions.
4. The first step which represents the dehydration of coordinated water is faster in Ni complex (E_a = 93 kJ mol^{-1}) than in Cu complex (E_a = 98 kJ mol^{-1}) (Figure 11a). The Cu complex is more stable than Ni complex (Figure 11b), which is indicated by the higher T_{max} value.
5. The chloride evolution starts at the first step in Ni complex and in the second step the Cu complex, in accordance with literature[31]. On the other side, the high value of T_{DTG} (211 °C) of Cu complex reflects its higher stability compared to Ni complex of T_{DTG} (132 °C).
6. Ni complex has a faster complete decomposition of its backbone (E_a = 131 kJ mol^{-1}) than Cu complex (E_a = 137 kJ mol^{-1}), making clear the higher stability of Cu complex.
7. The values of ΔG* for a given complex, generally, increase significantly for the subsequent decomposition steps, consequence of the increase of TΔS* values from one step to another which exceed the ΔH* values.

4. Conclusions

In this paper, some new complexes containing urea and asparagine ligands were prepared and characterized. The complexes have the following molecular formulae: $[M(L_1)(L_2)(H_2O)_n]Cl$ where M = Co(II), Ni(II) and Cu(II), L_1 = urea, and L_2 = asparagine. These complexes were characterized by elemental analysis, conductance measurements, IR, ^{1}HNMR and mass spectroscopy. Electronic spectra and magnetic measurements suggested an octahedral geometry for the complexes. Thermal analysis study showed faster decomposition reactions of the Ni complex and higher thermal stability of Cu complex.

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