



INFRARED SPECTROSCOPIC INVESTIGATIONS ON THE REACTION PRODUCTS RESULTED FROM THE INTERACTION BETWEEN SILVER(I) SALTS WITH UREA AT 90 °C

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ABSTRACT

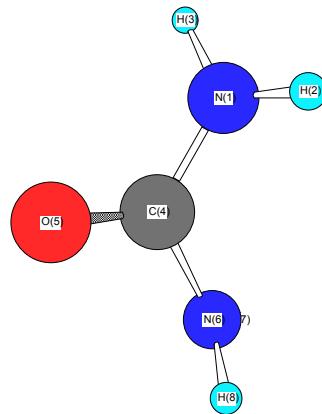
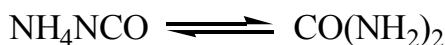
The ligational behavior of urea (U) with silver(I) salts like silver(I) chloride, silver(I) sulfate, silver(I) acetate, silver(I) nitrate, and silver(I) iodide at 90 °C temperature with 4-6 hrs has been studied by conductivity measurements, infrared spectra, scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), and x-ray powder diffraction (XRD). The high values of molar conductivity of the resulting urea complexes show them to be electrolytes in nature. The physical and spectral data were well explained in terms of the formation of $[\text{Ag}_2(\text{U})(\text{NCO})]\text{Cl} \cdot x\text{H}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{NO}_3 \cdot x\text{H}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{CH}_3\text{COO} \cdot x\text{H}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{SO}_4 \cdot x\text{H}_2\text{O}$, and $[\text{Ag}_2(\text{U})(\text{NCO})]\text{I} \cdot x\text{H}_2\text{O}$. On the basis of the infrared spectral data and the values of stretching vibrational bands of both $-\text{C}=\text{O}$ and $-\text{NH}_2$ groups, the complexation of metal ions toward urea was distinguished.

Keywords: Urea, Silver(I) salts, SEM, Conductance, Infrared spectra, XRD.

1-INTRODUCTION

Carbamide, carbonyldiamide or the most famous name, urea (Scheme 1), $\text{CH}_4\text{N}_2\text{O}$, was first prepared by Wöhler [1] by evaporating a solution containing a mixture of potassium isocyanate and ammonium

sulphate. Ammonium isocyanate, which is formed first, undergoes molecular rearrangement to give urea, as shown by the following reaction



Scheme 1: Structure of urea

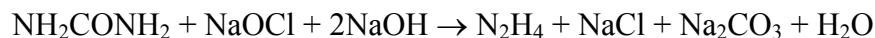
Urea may be prepared in the laboratory by the action of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. Industrially [2-4], urea is prepared by allowing liquid carbon dioxide and liquid ammonia to interact, and heating



Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Adults excrete about 30g of urea per day in the urine, from which it can be extracted by evaporating the urine to small volume and adding nitric acid, to give the slightly soluble urea nitrate, $\text{CO}(\text{NH}_2)_2\text{HNO}_3$. Urea has a melting point of 132°C, soluble in water and ethanol, but insoluble in ether. Urea is used for

the formed ammonium carbamate at 130-150 °C under about 35 atmospheric pressure. The carbamate is decomposed to form urea and water according to the following reaction.

preparing formaldehyde-Urea resin (plastics) [5], barbiturates [6], and fertilizers [7-10]. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of medicine [11-13]. Recently, urea is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite [6] e.g.



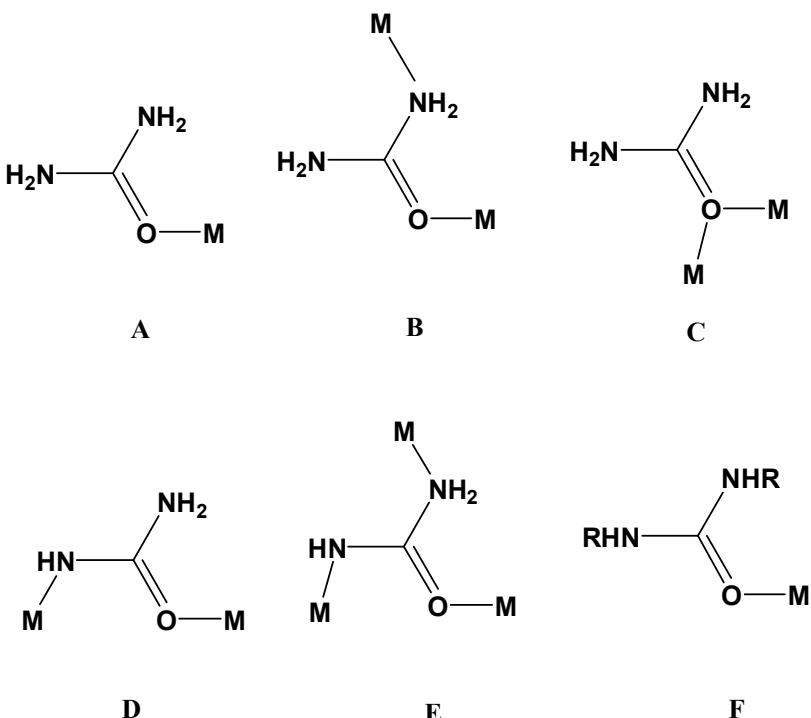
Urea is used in reactive dyeing [14] which has an effect on the formation and cleavage of covalent bond between the reactive dye and cellulose. The overall effect of urea on reactive dyeing depends on the solvolytic stability of the dye-fiber bond under specific dyeing conditions.

Complexes of urea with some metal ions are used as fertilizers [15-18]. Complexes of urea with zinc sulphate and nitrate, $[\text{Zn}(\text{CON}_2\text{H}_4)_6]\text{SO}_4\cdot\text{H}_2\text{O}$ and $[\text{Zn}(\text{CON}_2\text{H}_4)_4](\text{NO}_3)_2\cdot 2\text{H}_2\text{O}$ have very important application in this field [19]. These complexes were found to increase the yield of rice more than a dry mixture of urea-zinc salt does. Calcium nitrate-urea complex, $[\text{Ca}(\text{urea})_4](\text{NO}_3)_2$, [20,21] was used also as an adduct fertilizer. Some metal-urea complexes have pharmaceutical application, e.g., the platinum-urea complex which is used as antitumor [22].

Crystal structure studies have shown that in solid urea, both nitrogen atoms are identical. Bond length measurements [6] in urea give the C-N

distance as 1.37\AA° , while, in aliphatic amines the C-N bond length is 1.47\AA° . This indicates that the C-N bond in urea has some double bond character (about 28%).

Urea usually coordinates as a monodentate ligand through the oxygen atom, forming a $\text{C}=\text{O}\cdots\text{M}$ angle considerably smaller than 180° , in accordance with the sp^2 hybridization of the O atom (**A** in Scheme 2). The rare N,O-bidentate coordination mode (**B** in Scheme 2) has been found in a very limited number of cases [23, 24], while in $[\text{Hg}_2\text{Cl}_4\text{U}_2]$ each U molecule bridges the two Hg^{II} atoms through the oxygen atom [25] (**C** in Scheme 2). Of particular chemical/biological interest is the ability of U to undergo metal-promoted deprotonation [26]; the monoanionic ligand H_2NCONH^- adopts the $\mu 2$ (**D** in Scheme 2) and $\mu 3$ (**E** in Scheme 2) coordination modes. The urea and its derivatives such as the N,N'-dimethylurea and N,N'-diethylurea (Scheme 2) have only been found to coordinate as monodentate ligands through the oxygen atom (**F** in Scheme 2).



Scheme 2: The coordination modes of urea towards metal ions

Raman and infrared spectra of urea have been observed by several investigators [27-32]. The normal vibrations of the urea molecule were calculated by Kellner [33] on the assumption of the non-planar model. However, on the basis of the dichronic measurement of the infrared band arising from the N-H stretching vibration by Waldron and Badger [34] and the proton magnetic resonance absorption measurement made by Andrew and Hyndman [35], it is concluded that urea molecule has a planar structure. Yamaguchi et al. [36] calculated the normal vibrations of the C_{2v} model of urea molecule as an eight-body problem using a potential function of the Urey-Bradley force field and obtained the force constants which have been refined by the least-squares method. Based on the result of these calculations, Yamaguchi [36], assigned all of the observed frequencies in the spectra of urea and urea- d_4 . To the two vibrations of the frequencies 1686 and 1603cm^{-1} , there are considerable contributions of both CO stretching and NH_2 bending motions, whereas Stewart [37] assigned the 1686cm^{-1} band to CO stretching vibration and the 1603cm^{-1} band to NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686cm^{-1} , the

contribution of the NH_2 bending motion is greater than that of CO stretching motion. The band at 1629cm^{-1} corresponds to almost pure NH_2 bending vibration. The NH_2 bending motion of A_1 type is equal to that of B_2 type. The A_1 type band should have a frequency of about 1630cm^{-1} , if there is no coupling between NH_2 bending and CO stretching motions. On the other hand, the observed frequency of 1610cm^{-1} of urea- d_4 is assigned to almost pure skeletal vibration. Therefore, the interaction between the 1630 and 1610cm^{-1} vibration gives rise to the two observed bands at 1686 and 1603cm^{-1} . The infrared bands of urea- d_4 observed at 1245 and 1154cm^{-1} are assigned, respectively, to A_1 type and B_2 type, ND_2 bending vibrations. This assignment is consistent with the observed depolarization degrees of the Raman lines. The large frequency difference between the A_1 and B_2 vibrations is due to the fact that in the A_1 vibration, the cross term related to the CN stretching vibration is large.

The 1464cm^{-1} frequency of urea is assigned to the CN stretching vibration of B_2 type. The corresponding frequency of urea- d_4 is observed at 1490cm^{-1} . The 1150cm^{-1} band is assigned to NH_2 rocking vibrations of both A_1 and B_2 types. The

normal vibration calculation yields almost the same values for these frequencies.

Urea possesses two types of potential donor atoms, the carbonyl oxygen and amide nitrogens. Penland et al. [38] studied the infrared spectra of urea complexes to determine whether coordination occurs through oxygen or nitrogen atoms. The electronic structure of urea may be represented by a resonance hybrid of structures **A-F** as shown in scheme 1 with each contributing roughly an equal amount. If coordination occurs through nitrogen, contributions of structure **B** will decrease. This results in an increase of the CO stretching frequency with a decrease of CN stretching frequency. The N-H stretching frequency in this case may fall in the same range as those of the amido complexes. If coordination occurs through oxygen, the contribution of structure (**A**) will decrease. This may result in a decrease of the CO stretching frequency but no appreciable change in NH stretching frequency. Since the vibrational spectrum of urea itself has been analyzed completely [36], band shifts caused by coordination can be checked immediately. For example, the effect of the coordination on the spectra

of the complexes of urea with pt(II) and Cr(III) in which the coordination occurs through nitrogen and oxygen atoms, respectively [38]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pd(II) coordinates to the nitrogen, whereas Fe(III) , Zn(II) , and Cu(II) coordinate to the oxygen of urea [38].

In urea-metal complexes, if a nitrogen-to-metal bond is present, the vibrational spectrum of this complex differs significantly from that of the free urea molecule. The N-H stretching frequencies would be shifted to lower values, and the C=O bond stretching vibration, ($\nu(\text{C=O})$) would be shifted to higher frequency at about 1700cm^{-1} [39].

Recently, urea represents not only an important molecule in biology [40] but also an important raw material in chemical industry [41]. The aim of this publication is to report the synthesis, characterization, conductance and morphological behavior of the resulting compounds formed from the reactions of urea with silver(I) chloride, silver(I) sulfate, silver(I) acetate, silver(I) nitrate, and silver(I) iodide at $90\text{ }^{\circ}\text{C}$ and ignition $800\text{ }^{\circ}\text{C}$ temperature.

2-EXPERIMENTAL

2-1- Materials

Urea, AgCl , Ag_2SO_4 , AgCH_3COO , AgNO_3 , and AgI were obtained from Aldrich Company. Urea was received from Fluka chemical company. All chemicals used in this study were of analytically reagent grade and used without further purification.

2-2- Synthesis of silver isocyanate urea complexes

The urea complexes, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{Cl}\cdot\text{xH}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\cdot\frac{1}{2}\text{SO}_4\cdot\text{xH}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{CH}_3\text{COO}\cdot\text{xH}_2\text{O}$, $[\text{Ag}_2(\text{U})(\text{NCO})]\text{NO}_3\cdot\text{xH}_2\text{O}$, and $[\text{Ag}_2(\text{U})(\text{NCO})]\text{I}\cdot\text{xH}_2\text{O}$, were prepared as a 25 mL volume of urea solution (6.0g, 0.1 mole) was mixed with an equal volume of AgCl , Ag_2SO_4 , AgCH_3COO , AgNO_3 , or AgI salts solution, AgCl , (1.44 g, 0.01 mole), Ag_2SO_4 (3.12 g, 0.01 mole), AgCH_3COO (1.67 g, 0.01 mole), AgNO_3 (1.70 g, 0.01 mole) or AgI (2.35 g, 0.01 mole) in 25 mL distilled water. The mixtures were stirred for about 1 hr then heated to $90\text{ }^{\circ}\text{C}$ for 4-6 hours on a water

bath under refluxed system. The precipitated products were filtered off, dried at $60\text{ }^{\circ}\text{C}$ in an oven for 3 hours and then dried under *vacuo* over anhydrous calcium chloride.

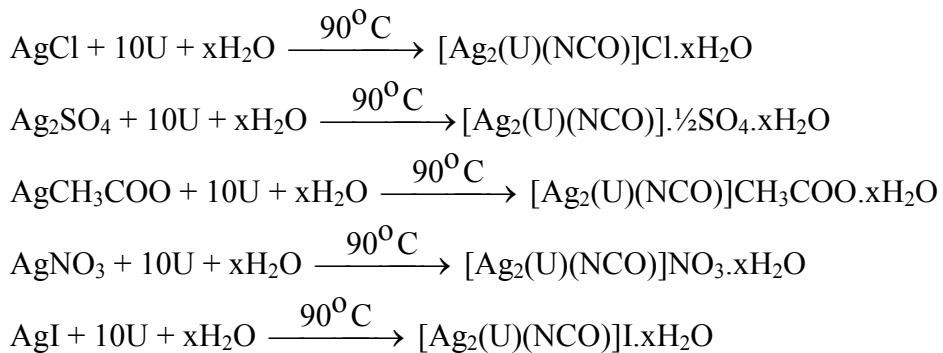
2-3- Measurements

The molar conductivities of freshly prepared $1.0\times 10^{-3}\text{ mol/cm}^3$ dimethylsulfoxide (DMSO) solutions were measured for the soluble urea complexes using Jenway 4010 conductivity meter. The infrared spectra with KBr discs were recorded on a Shimadzu FT-IR Spectrophotometer (4000–400 cm^{-1}). Scanning electron microscopy (SEM) images and Energy Dispersive X-ray Detection (EDX) were taken in Joel JSM-6390 equipment, with an accelerating voltage of 20 KV. The X-ray diffraction patterns for the urea complexes were recorded on X 'Pert PRO PANalytical X-ray powder diffraction, target copper with secondary monochromate.

3- RESULTS AND DISCUSSION

The color, physical characteristic, molecular weight data, formula weight, and molar conductance measurements of silver(I) urea complexes are given in Table 1. The formula weight data of the prepared complexes revealed 1:2 molar

ratio (U: Ag) and good agreement with the general formulas $[Ag_2(U)(NCO)]Cl.xH_2O$, $[Ag_2(U)(NCO)].\frac{1}{2}SO_4.xH_2O$, $[Ag_2(U)(NCO)]CH_3COO.xH_2O$, $[Ag_2(U)(NCO)]NO_3.xH_2O$ and $[Ag_2(U)(NCO)]I.xH_2O$ complexes. The reactions can be represented by the stoichiometric equations:



The complexes are hygroscopic, high melting points, soluble in dimethylsulfoxide, DMSO. The molar conductivities of 10^{-3} mol dm $^{-3}$ solutions of the prepared complexes in DMSO (Table 1) indicate that the complexes have an electrolytic nature.

3-1- Molar conductance measurements

The molar conductivity values for the urea complexes in DMSO solvent (10^{-3} mol dm $^{-3}$) are exhibited in the range of (83–122) $\Omega^{-1} cm^2 mol^{-1}$, suggesting them to be electrolytes (Table 1). Conductivity measurements have frequently been used in structural of metal complexes (mode of coordination) within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molar ions that a

complex liberates in solution (in case of presence anions outside the coordination sphere), the higher will be its molar conductivity and vice versa. It is clear from the conductivity data that the complexes present seem to be electrolytes. Also the molar conductance values indicate that the anions present outside the coordination sphere. This result was confirmed from the elemental analysis data where Cl^- , SO_4^{2-} , CH_3COO^- , NO_3^- and I^- ions are precipitated with colored solution by adding of respective reagents solutions, this experimental test is a good matched with CHN data. All these complexes have electrolytic properties. This fact elucidated that the anions are present. These results establish the stoichiometry of these complexes, which are in agreement with the general formulas suggested.

Table 1: Physical characterization, micro-analytical and molar conductance data of silver(I) urea complexes

Complexes Molecular formula	Color	Molar ratio	Molecular weight g/mol	Λ_m ($\Omega^{-1} cm^2 mol^{-1}$)
$[Ag_2(U)(NCO)]Cl.xH_2O$	Gray	1:1	365	101
$[Ag_2(U)(NCO)].\frac{1}{2}SO_4.xH_2O$	Gray	1:1	376	122
	Gray	1:1	390	83

[Ag₂(U)(NCO)]CH₃COO.xH₂O

[Ag ₂ (U)(NCO)]NO ₃ .xH ₂ O	Gray	1:1	393	114
[Ag ₂ (U)(NCO)]I.xH ₂ O	Yellow	1:1	460	96

3-2- Infrared spectra

The infrared spectra of the silver(I) urea complexes at room 90 °C and 800 °C temperature are shown in Figs. 1 and 2, respectively. The band locations were measured for the mentioned silver(I)-urea complexes, together with the proposed assignments for the most characteristic vibrations are presented in Table 2. In order to facilitate the spectroscopic analysis and to put our hand on proper structure of the prepared complexes, the spectra of the silver(I)-urea complexes were accurately compared with those of the urea and similar complexes in literature survey. The infrared spectra in the wide frequency range (4000–400 cm⁻¹) are shown in Fig. 1, whereas the region between 1500–to-400 cm⁻¹ is focused to silver(I)-urea complexes at 800 °C temperatures (Fig. 2). The discussion of the spectra will be addressed on the basis of the most characteristic vibrations. The assignments of full vibrational analysis of crystalline urea have been published [38]. Table 2 gives diagnostic infrared peaks of the free urea ligand, published work and five Ag(I) urea complexes. Assignments have been given in

comparison with the data obtained for the free urea, that is, coordinated, U [38] and its [Pt(urea)₂Cl₂] and [Cr(urea)₆]Cl₃ complexes [38]. The effect of the coordination on the spectra of the complexes of urea with [Pt(urea)₂Cl₂] and [Cr(urea)₆]Cl₃ complexes in which the coordination occurs through nitrogen and oxygen atoms, respectively [38]. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pd(II) ions in [Pt(urea)₂Cl₂] coordinate to the nitrogen, whereas Fe(III), Zn(II), and Cu(II) coordinate to the oxygen of urea [38]. The distinguished bands of ν (C–N) are exhibited at lower wavenumbers in the spectra of [Ag₂(U)(NCO)]Cl₂.xH₂O, [Ag₂(U)(NCO)].½SO₄.xH₂O, [Ag₂(U)(NCO)]CH₃COO.xH₂O, [Ag₂(U)(NCO)]NO₃.xH₂O and [Ag₂(U)(NCO)]I.xH₂O complexes than for free urea, whereas the ν (C=O) band shows a frequency at the same wavenumber of free urea. These shifts are consistent with nitrogen coordination, suggesting the presence of $+N=C=O^-$ resonance features [42], see Scheme 3.

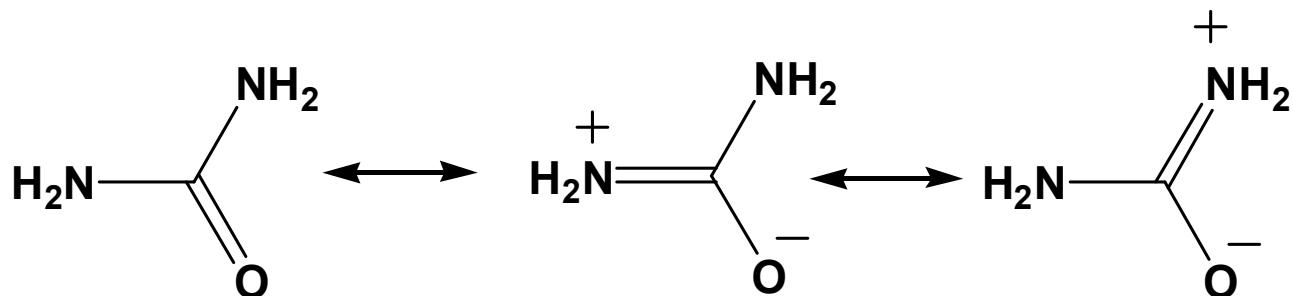
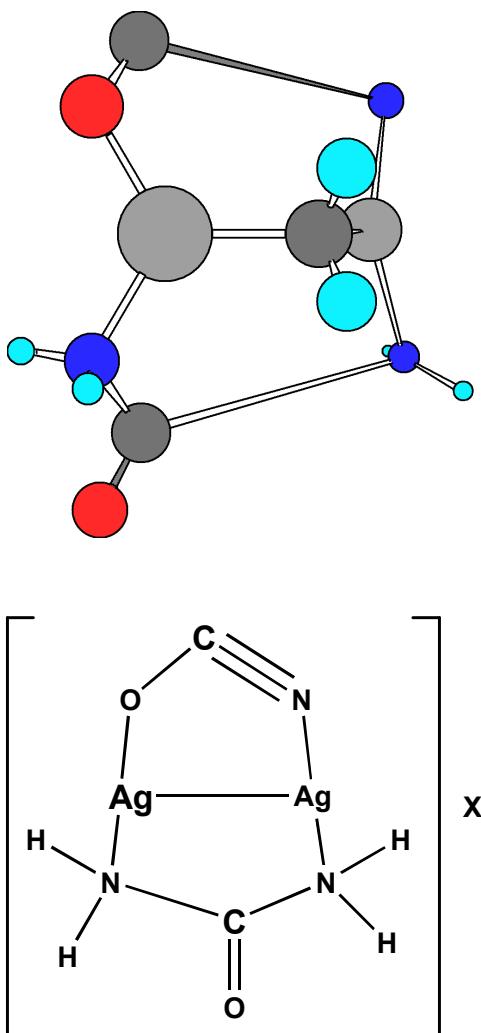
**Scheme 3: Resonance types of urea**

Table 2: Characteristic infrared frequencies (cm^{-1}) and tentative assignments of urea (U), $[\text{Pt}(\text{urea})_2\text{Cl}_2]$ (A), $[\text{Cr}(\text{urea})_6]\text{Cl}_3$ (B), $[\text{Ag}_2(\text{U})(\text{NCO})]\text{Cl}_x\text{H}_2\text{O}$ (1), $[\text{Ag}_2(\text{U})(\text{NCO})]\text{NO}_3\text{.xH}_2\text{O}$ (2), $[\text{Ag}_2(\text{U})(\text{NCO})]\text{CH}_3\text{COO.xH}_2\text{O}$ (3), $[\text{Ag}_2(\text{U})(\text{NCO})]\text{NO}_3\text{.xH}_2\text{O}$ (4) and $[\text{Ag}_2(\text{U})(\text{NCO})]\text{I.xH}_2\text{O}$ (5) complexes

U	A	B	1	2	3	4	5	Assignments ^(b)
3450	3390	3440	3450	3450	3470	3444	3452	$\delta_{\text{as}}(\text{NH}_2)$
	3290	3330		3347	3347	3353	3351	
3350	3130	3190	3211	3174	3217	3198	3192	$\delta_{\text{s}}(\text{NH}_2)$
		3030						
---	---	---	2247	2241	2163	2247	2245	$\delta(\text{NCO})$
				2163	2163	2163	2162	
1683	1725	1505	1672	1672	1672	1665	1673	$\delta(\text{C=O})$
				1627	1620	1620	1614	$\delta(\text{H}_2\text{O})$
								$\delta(\text{H}_2\text{N})$
1471	1395	1505	1459	1453	1559	1453	1457	$\delta(\text{C-N})$

The band related to the stretching vibration $\nu(\text{O-H})$ of uncoordinated H_2O is observed as expected in the range of (3400-3450) cm^{-1} , while the corresponding bending motion of the uncoordinated water, $\delta(\text{H}_2\text{O})$, is observed in the range of (1630-1638) cm^{-1} . The infrared spectrum of the silver(I) urea products, Fig. 1, clearly indicate the formation of the (NCO^-) group with its characteristic $\nu(\text{N}\equiv\text{C})$ at 2240 and 2150 cm^{-1} [43] resulted from the combination between ($\text{NH}_3^+ + \text{CO}_3^-$) at high temperature [44]. The one IR-active $\nu(\text{M-N})$ vibration of silver urea complexes presence at around 490-500 [45]. Three bands with strong-to-weak intensities occur in the region above 1000 cm^{-1} at 1200, 1122 and 990 cm^{-1} are assigned to the different symmetric and antisymmetric bond vibrations, $\nu(\text{SO}_4)^{2-}$, while the bending motion of $\delta(\text{SO}_4)^{2-}$ is assigned to the band at 618 cm^{-1} . In the

silver urea complexes, the characteristic stretching vibrations of the nitrate group, NO_3^- , is observed at around (1388 and 1200 cm^{-1} attributed to $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$, respectively [45]. The stretching motion of ($\nu(\text{N=O})$) is observed at 1453 cm^{-1} as a strong band, while the bending motion of the type $\delta(\text{NO}_2)$ are well resolved and observed at 786 as a medium band. The ν_{as} and ν_{s} carboxylate stretching of silver(I) acetate urea complex are seen at 1620 cm^{-1} and 1400 cm^{-1} , respectively, with $\Delta\nu$ is in between 206 – 257 cm^{-1} , showing the unidentate coordination [45] of carboxylate ions. According to this result, it can be deduced that the electronic environments of the urea protons change with the formation of the new complexes and suggest the following chelations (scheme 4).



Scheme 4: Suggested structure of silver(I) urea complexes

3-3- X-ray powder diffraction studies

The x-ray powder diffraction patterns for the $[\text{Ag}_2(\text{U})(\text{NCO})]\text{NO}_3 \cdot x\text{H}_2\text{O}$ and Ag metal as a final residual product after ignited of parent silver(I) urea complex are depicted in Fig. 3. Inspecting these patterns, it notice that silver(I) urea system is well crystalline but for diagram of silver(I) complex at 800 °C. The crystallite size of these complexes could be estimated from XRD patterns by applying FWHM

of the characteristic peaks using Deby-Scherrer equation 1 [46]. Where D is the particle size of the crystal gain, K is a constant (0.94 for Cu grid), λ is the x-ray wavelength (1.5406 Å), θ is the Bragg diffraction angle and β is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. These data gave an impression that the particle size located within nano scale range.

$$D = K\lambda/\beta \cos\theta \quad (\text{Deby-Scherrer equation})$$

3-4- SEM and EDX studies

Scanning electron microscopy (SEM) is a simple tool used to give an impression about the microscopic aspects of the physical behavior of urea

as a chelating agent (Fig. 4). Although this tool is not a qualified method to confirm complex formation but it can be a reference to the presence of a single component in the synthetic complexes. The pictures

of the $[Ag_2(U)(NCO)]NO_3 \cdot xH_2O$ and Ag metal as a final residual product after ignited of parent silver(I) urea complex show a small particle size with an nano feature products. The chemical analysis results by EDX for the formed complexes show a homogenous distribution in between metal ions and chelating agent. SEM examinations were checked the morphology of the surfaces of these complexes that

show small particles which tendency to agglomerates formation with different shapes comparison with the start materials. The peaks of EDX profile of these complexes (Fig. 5) refer to all elements which constitute the molecules of silver(I) urea complex that clearly identified confirming the proposed structures.

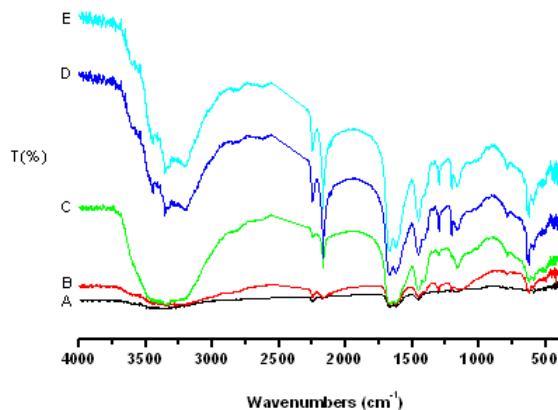


Figure. 1: Infrared spectra of silver(I) urea complexes: $[Ag_2(U)(NCO)]Cl \cdot xH_2O$ (A), $[Ag_2(U)(NCO)] \cdot \frac{1}{2}SO_4 \cdot xH_2O$ (B), $[Ag_2(U)(NCO)]CH_3COO \cdot xH_2O$ (C), $[Ag_2(U)(NCO)]NO_3 \cdot xH_2O$ (D) and $[Ag_2(U)(NCO)]I \cdot xH_2O$ (E) complexes

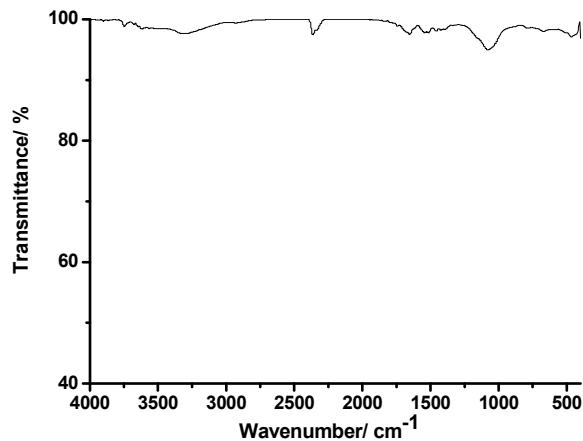


Figure. 2: Infrared spectra of $[Ag_2(U)(NCO)]NO_3 \cdot xH_2O$ complex at $800^{\circ}C$ (Ag metal).

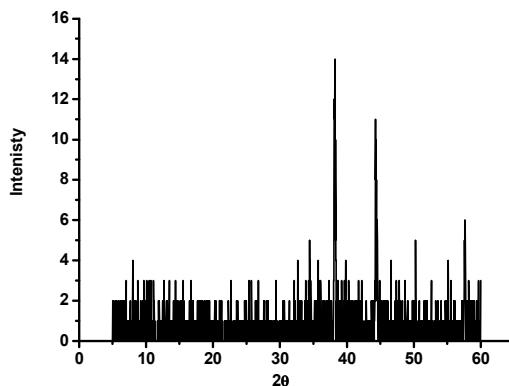


Figure. 3: XRD spectrum of the $[Ag_2(U)(NCO)]NO_3.xH_2O$ complex at $800^{\circ}C$ (Ag metal).

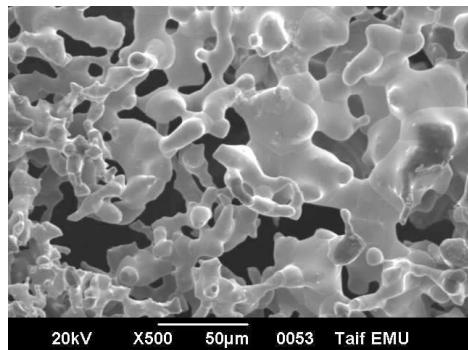


Figure. 4: SEM image of the $[Ag_2(U)(NCO)]NO_3.xH_2O$ complex at $800^{\circ}C$ (Ag metal).

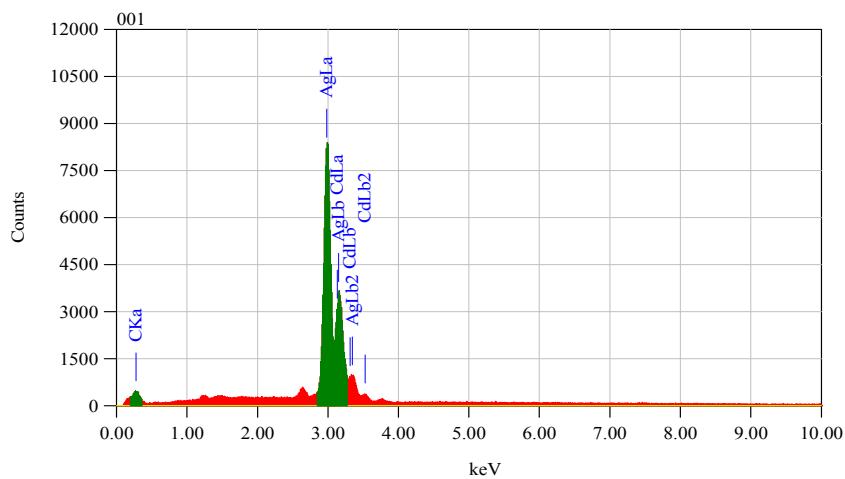


Figure. 5: EDX diagram of the $[Ag_2(U)(NCO)]NO_3.xH_2O$ complex at $800^{\circ}C$ (Ag metal).

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