



SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF UREA METAL COMPLEXES WITH Cu(II), Zn(II), Ag(I), Cd(II) AND Hg(II) IONS AT HIGH TEMPERATURE

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ABSTRACT

In the present study, urea metal complexes formed in the reaction of urea (U) with Cu(II), Zn(II), Ag(I), Cd(II) and Hg(II) ions have been investigated at 90°C. These were characterized through electronic and infrared spectra as well as elementally, magnetically and conductively analysis. The obtained results showed that the formed complexes have the formulas $(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$, $(\text{ZnCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$, $\text{AgNO}_3 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$, $(\text{CdCl}_2)_2 \cdot \text{U} \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ and $(\text{HgCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ in full agreement with the known reaction stoichiometries as well as the elemental measurements. The high values of molar conductivity of some of the resulting urea complexes show them to be electrolytes in nature.

Key words: Urea, Metal complexes, High temperature, Elemental analyses, Conductance.

INTRODUCTION

Carbamide, carbonyldiamide or the most famous name, urea ($\text{CH}_4\text{N}_2\text{O}$) was first prepared by Wöhler¹ by evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate. Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea has a melting point of 132°C, soluble in water and ethanol, but insoluble in ether. Urea is used for preparing formaldehyde-Urea resin (plastics)², barbiturates³, and fertilizers⁴⁻⁷. 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 medicine⁸⁻¹⁰. Complexes of urea with some metal ions are used as fertilizers¹¹⁻¹⁴. Some metal-urea complexes have pharmaceutical application, e.g., the platinum-urea complex, which is used as antitumor¹⁵. Raman and infrared spectra of urea

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have been observed by several investigators. The normal vibrations of the urea molecule were calculated by Kellner¹⁶ 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 Badger¹⁷ and the proton magnetic resonance absorption measurement made by Andrew and Hyndman¹⁸. It is concluded that urea molecule has a planar structure. Yamaguchi et al.¹⁹ 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 et al.¹⁹ assigned all of the observed frequencies in the spectra of urea and urea-d₄. To the two vibrations of the frequencies 1686 and 1603 cm^{-1} , there are considerable contributions of both CO stretching and NH_2 bending motions, whereas Stewart²⁰ assigned the 1686 cm^{-1} band to CO stretching vibration and the 1603 cm^{-1} band to NH_2 bending motion. Urea possesses two types of potential donor atoms, the carbonyl oxygen and amide nitrogens. Penland et al.²¹ studied the infrared spectra of urea complexes to determine whether coordination occurs through oxygen or nitrogen atoms. 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, ($\nu(\text{C}=\text{O})$) would be shifted to higher frequency at about 1700 cm^{-1} .²² The aim of this work is to synthesis and characterize the resulting complexes formed from the reactions of urea with AgNO_3 , $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and ZnCl_2 at 90°C.

EXPERIMENTAL

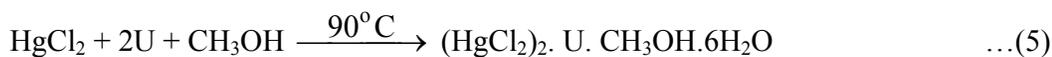
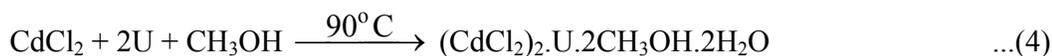
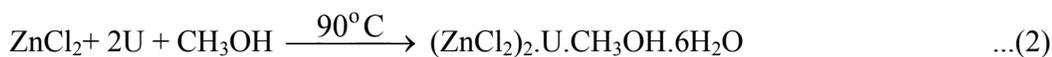
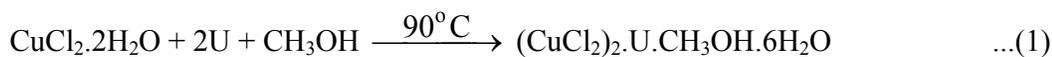
Material and methods

Urea, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , AgNO_3 , $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, HgCl_2 and methanol 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. The complexes, $(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (**1**), $(\text{ZnCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (**2**), $\text{AgNO}_3 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**3**) $(\text{CdCl}_2)_2 \cdot \text{U} \cdot 2\text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**4**), $(\text{HgCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (**5**) were prepared by mixing equal methanolic solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.70 g, 0.01 mole), ZnCl_2 (1.36 g, 0.01 mol), AgNO_3 (1.70 g, 0.01 mole), HgCl_2 (2.72 g, 0.01 mole), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (2.01 g, 0.01 mole) in 25 mL methanol with a 50 mL volume of urea solution (1.2 g, 0.01 mole) in methanol solvent. The mixtures were stirred for about 12 hrs under refluxed system at 90°C. The Ag(I), Cd(II) and Zn(II)-urea complexes took a longer time to precipitate. The amount of the formed precipitate increased with standing time. The complexes formed were filtered off, dried under *vacuo* over anhydrous calcium chloride. The elemental analyses of carbon, hydrogen and nitrogen contents were performed by the microanalysis unit at Cairo

University, Egypt, using a Perkin-Elmer CHN 2400 (USA). The molar conductivities of freshly prepared 1.0×10^{-3} mol/cm³ dimethylsulfoxide (DMSO) solutions were measured for the soluble urea complexes using Jenway 4010 conductivity meter. Magnetic measurements were performed on the Magnetic Susceptibility Balance, Sherwood Scientific, and Cambridge Science Park-Cambridge-England. The infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer (4000-400 cm⁻¹). The electronic absorption spectra of urea complexes were recorded within 1000-200 nm range using UV2 Unicam UV/Vis Spectrophotometer fitted with a quartz cell of 1.0 cm path length.

RESULTS AND DISCUSSION

The elemental analysis data (Table 1) of the prepared complexes revealed 1:1 molar ratio (M:U) for all complexes are in a good agreement with the general formulas (CuCl₂)₂.U.CH₃OH.6H₂O (**1**), ZnCl₂.U.CH₃OH.4H₂O (**2**), AgNO₃.U.CH₃OH.2H₂O (**3**), (CdCl₂)₂.U.CH₃OH.2H₂O (**4**) and (HgCl₂)₂.U.CH₃OH.6H₂O (**5**). The reactions can be represented by the stoichiometric equations:



The molar conductivities of the complex solution prepared in DMSO (10^{-3} g/5 mL) (Table 1) indicate that some of the complexes have an electrolytic nature. The molar conductivity values for the urea complexes in DMSO solvent are in the range of (18-335) $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, 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. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance according to the Gouy method. The magnetic moments of $(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (**1**) complex at $T = 300 \text{ K}$ and its corresponding hybrid orbitals was calculated. The observed value of the effective magnetic moments μ_{eff} measured for the complex was 1.83 B.M. this is in convenient with experimental value of 1.85 B. M. obtained for planar $\text{Cu}(\text{II})$ complex with dsp^2 hyperdization²³. The UV-visible spectra of the urea complexes given in Table 2, and the absorption bands of the metal ions in the spectra were assigned.

Table 1: Physical characterization, micro-analytical data of urea complexes

Complexes empirical formula (MW.)	Color	Molar ratio	Elemental analysis (%), Found (Calcd.)		
			C	H	N
$(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (1) 468.96 g/mol	Green	1:1	05.23 (05.11)	04.26 (04.26)	04.90 (05.97)
$(\text{ZnCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (2) 472.58 g/mol	White	1:1	04.70 (05.07)	04.10 (04.23)	05.41 (05.92)
$\text{AgNO}_3 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (3) 297.87 g/mol	Black	1:1	08.18 (08.06)	04.28 (04.03)	13.76 (14.10)
$(\text{CdCl}_2)_2 \cdot \text{U} \cdot 2\text{Me} \cdot 2\text{H}_2\text{O}$ (4) 526.64 g/mol	White	1:1	06.37 (06.84)	03.42 (03.04)	05.63 (05.32)
$(\text{HgCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (5) 743 g/mol	White	1:1	03.19 (03.23)	02.53 (02.69)	03.78 (03.77)

Table 2: Molar conductance and magnetic moment data of urea complexes

Complex	Λ_m , ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	μ_{eff}	Electronic spectra	
			Bands	Assignments
$(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (1)	93	1.83	291	$\pi-\pi^*$
$(\text{ZnCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (2)	28	-	239	$\pi-\pi^*$
$\text{AgNO}_3 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (3)	425	-	262	$\pi-\pi^*$
$(\text{CdCl}_2)_2 \cdot \text{U} \cdot 2\text{Me} \cdot 2\text{H}_2\text{O}$ (4)	34	-	250	$\pi-\pi^*$
$(\text{HgCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (5)	41	-	269	$\pi-\pi^*$

The infrared spectra of the Cu(II), Zn(II), Ag(I), Cd(II), Hg(II) and urea complexes at room temperature are shown in Fig. 1 and their characteristic vibrations are presented in Tables 3 and 4. Tables 3 and 4 give diagnostic infrared peaks of the free urea ligand, published work and Ag(I), Cr(III), Cd(II) and Zn(II) complexes. Assignments have been given in comparison with the data obtained for the free urea, that is, uncoordinated, U²¹ and its [Pt(urea)₂Cl₂] and [Cr(urea)₆]Cl₃ complexes²¹.

Table 3: Characteristic infrared frequencies (cm⁻¹) and tentative assignments of urea (U), (CuCl₂)₂.U.Me.6H₂O (1), (ZnCl₂)₂.U.Me.6H₂O (2) and AgNO₃.U.Me.2H₂O (3) complexes

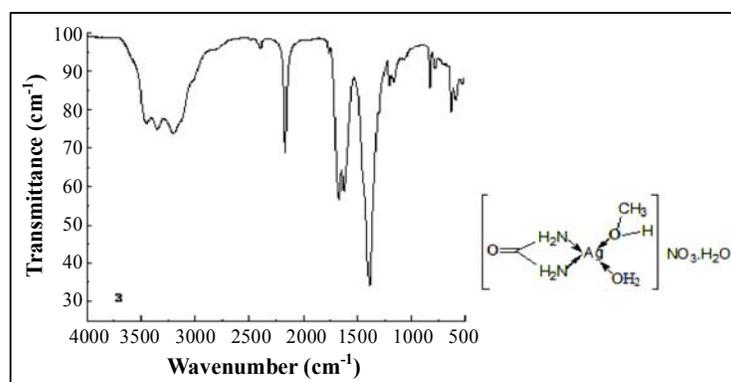
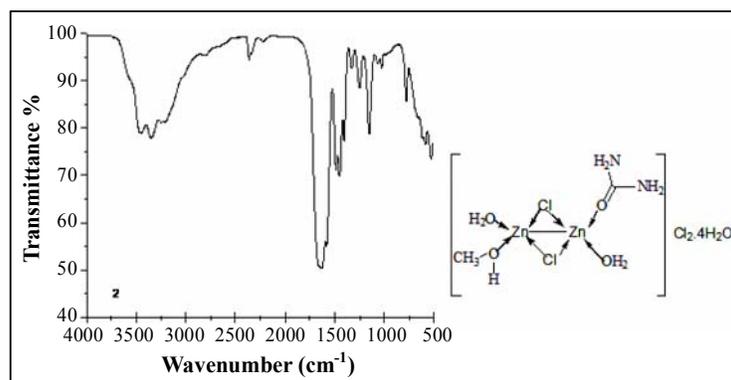
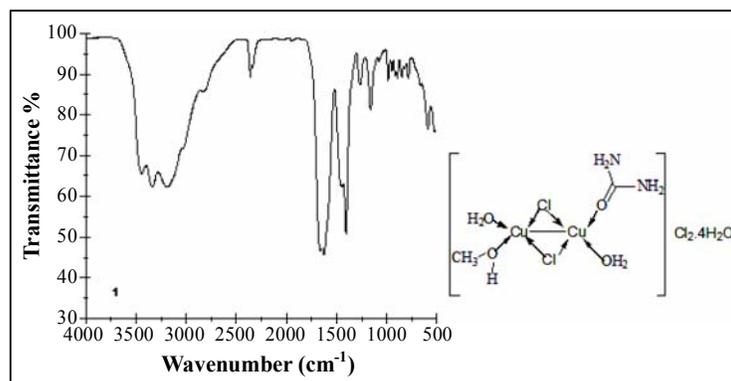
U	A	B	1	2	3	Assignments ^(b)
3450	3390	3440	3447	3457	3447	v _{as} (NH ₂)
	3290	3330	3336	3354	3351	v(OH); CH ₃ OH
3350	3130	3190	3195	33247	321	v _s (NH ₂)
	3030					v(CH ₃); CH ₃ OH
1683	1725	1505	1624	1627	1763	δ(C=O)
1471	1395	1505	1403	1405	1386	v(C-N)

Table 4: Characteristic infrared frequencies (cm⁻¹) and tentative assignments of urea (U), (CdCl₂)₂.U.2Me.2H₂O (4) and (HgCl₂)₂.U.Me.6H₂O (5) complexes

U	A	B	4	5	Assignments ^(b)
3450	3390	3440	3466 3418	3461 3355	v _{as} (NH ₂)
	3290	3330			v(OH); CH ₃ OH
3350	3130	3190	3341	3204	v _s (NH ₂)
	3030				v(CH ₃); CH ₃ OH
1683	1725	1505	1631	1613	δ(H ₂ O)
					δ(C=O)
1471	1395	1505	1456	1446	v(C-N)

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. 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. The distinguished bands of $\nu(\text{C-N})$ are exhibited at lower wavenumbers in the spectra of $\text{AgNO}_3 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (**3**) complex than for free urea, whereas the $\nu(\text{C=O})$ band shows a frequency at nearly the same wavenumber of free urea. These shifts are consistent with nitrogen coordination, suggesting the presence of $+\text{N}=\text{C}-\text{O}-$ resonance features²⁴.



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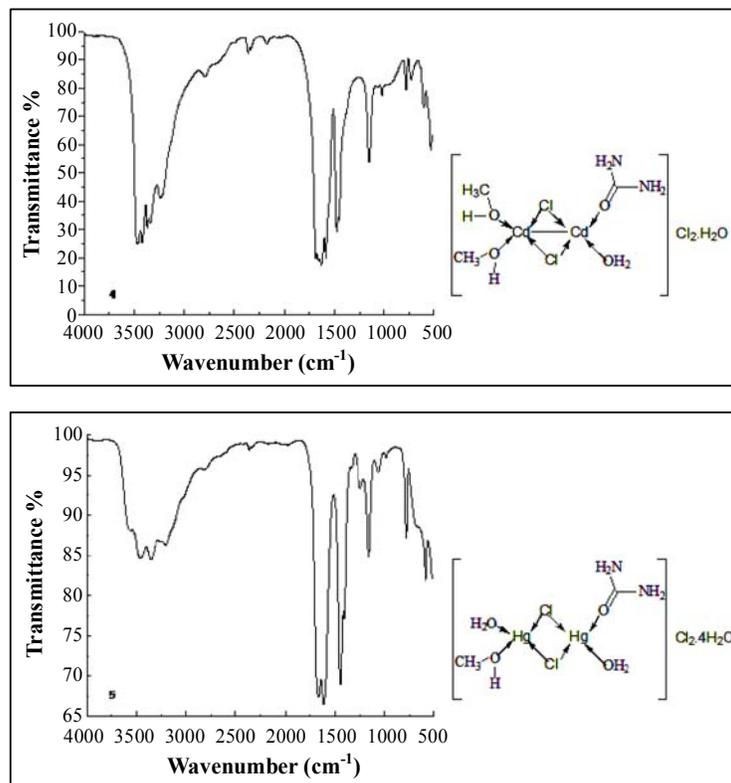


Fig. 1: Infrared spectra of urea complexes: $(\text{CuCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (1), $(\text{ZnCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (2), $\text{AgNO}_3 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (3), $(\text{CdCl}_2)_2 \cdot \text{U} \cdot 2\text{Me} \cdot 2\text{H}_2\text{O}$ (4) and $(\text{HgCl}_2)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (5)

Concerning, $\text{CuCl}_2 \cdot 2\text{U} \cdot \text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (1), $\text{ZnCl}_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (2), $\text{CdCl}_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 4\text{H}_2\text{O}$ (4), and $\text{HgCl}_2 \cdot \text{U} \cdot \text{CH}_3\text{OH} \cdot 6\text{H}_2\text{O}$ (5) complexes, the coordination mode take place *via* oxygen of amide group, the positively charged metal ion stabilizes the negative charge on the oxygen atom; the NCO group now occurs in its polar resonance form and the double bond character of the CN bond increases or still not affected, while the double bond character of the CO bond decreases, resulting in an increase of the CN stretching frequency with a simultaneous decrease in the CO stretching frequency^{25,26}. The one IR-active $\nu(\text{M}-\text{O})$ vibration of Cr(III), Cd(II) and Zn(II) urea complexes presence at 442, 473, and 443 cm^{-1} ^{24,25}. The band related to the stretching vibration $\nu(\text{O}-\text{H})$ 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} . In silver complex, the coordination mode take place *via* nitrogens of amide group, the characteristic stretching vibrations of the nitrate group, NO_3^- , is observed at around (1385 and 1160 cm^{-1}

attributed to $\nu_{as}(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$, respectively²⁷. The stretching motion of ($\nu(\text{N}=\text{O})$) is observed at 1461 cm^{-1} as a strong band, while the bending motion of the type $\delta(\text{NO}_2)$ are well resolved and observed at 783 as a medium band.

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