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The Chelating Behavior of Urea Complexed with the Metal Ions of Copper (II), Zinc (II), Silver (I), Cadmium (II) and Mercury (II) at Room Temperature.

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ABSTRACT

The chelating behavior of urea (U) complexed with copper(II), zinc(II), silver(I), cadmium(II) and mercury(II) ions at room temperature has been studied by elemental analyses, magnetic susceptibility, conductivity measurements, infrared and UV-visible spectroscopy. Some of the formed complexes show high values of molar conductivity, indicating these complexes are electrolytes in nature. The obtained complexes can be formulated as $CuCl_2.2U.CH_3OH.4H_2O$, $ZnCl_2.U.CH_3OH.4H_2O$, $AgNO_3.U.CH_3OH.6H_2O$, $CdCl_2.U.CH_3OH.4H_2O$ and $HgCl_2.U.CH_3OH .6H_2O$.

Keywords: Chelating behavior of urea, Conductivity measurements, Magnetic susceptibility, Spectroscopic studies.

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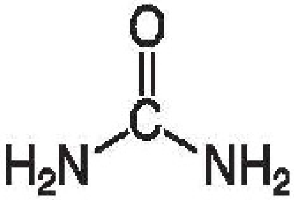
INTRODUCTION

Carbamide, carbonyldiamide or the most famous name, urea (Scheme 1), CH_4N_2O, was first prepared by Wöhler [1] by evaporating a solution containing a mixture of potassium isocyanate and ammonium sulphate.



Scheme 1: Structure of urea

Industrially [2-4], urea is prepared by allowing liquid carbon dioxide and liquid ammonia to interact, and heating 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;

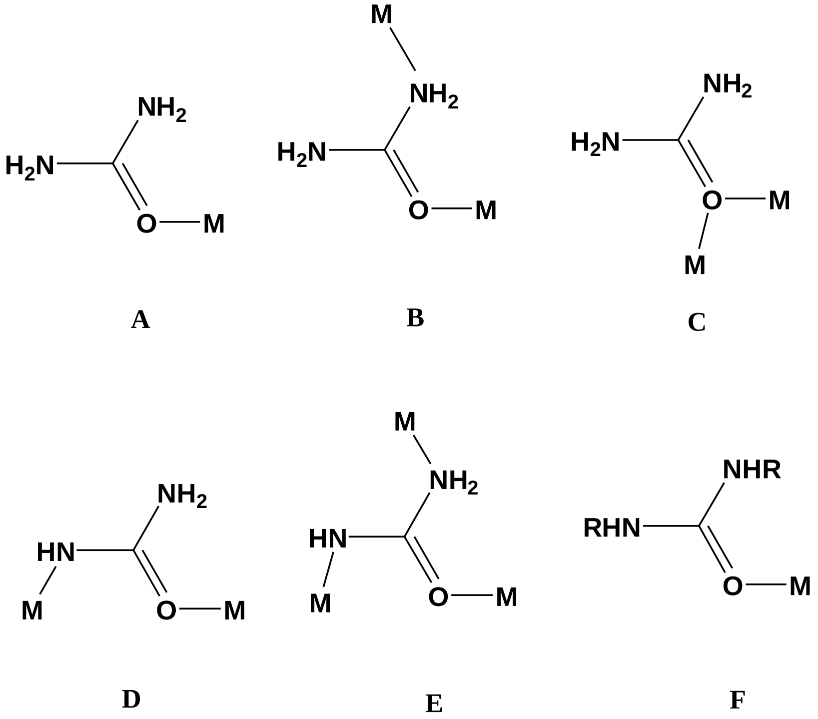
$$2NH_3 + CO_2 \rightarrow NH_2\,COONH_4 \rightarrow CO(NH_2)_2 + H_2O$$

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, $CO(NH_2)_2.HNO_3$. 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) [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.,

$$NH_2CONH_2 + NaOCl + 2NaOH \rightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

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, $[Zn(CON_2H_4)_6]SO_4.H_2O$ and $[Zn(CON_2H_4)_4](NO_3)_2.2H_2O$ 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, $[Ca(urea)_4](NO_3)_2$, [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 1.37A^o, while, in aliphatic amines the C-N bond length is 1.47A^o. 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 $C{=}O\cdot\cdot\cdot M$

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 $[Hg_2Cl_4U_2]$ 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 decreases. 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, (ν(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]. This work aimed to prepare and investigate the resulting compounds formed from the reactions of urea with $AgNO_3$, $CrCl_3.6H_2O$, $CdCl_2.H_2O$ and $ZnCl_2$ at room temperature.

MATERIAL AND METHODS

Synthetic procedure

Urea, $CuCl_2.2H_2O$, $ZnCl_2$, $AgNO_3$, $CdCl_2.H_2O$, $HgCl_2$ 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, $CuCl_2.2U.CH_3OH.4H_2O$ (**1**), $ZnCl_2.U.CH_3OH.\ 4H_2O$ (**2**), $AgNO_3.U.CH_3OH.6H_2O$ (**3**), $CdCl_2.U.CH_3OH.4H_2O$ (**4**), $HgCl_2.U.CH_3OH\ .6H_2O$ (**5**) were prepared by mixing equal methanolic solutions of $CuCl_2.2H_2O$ (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), 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 hours under refluxed system at room temperature *Ca*. 25 °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 time of standing. The complexes formed were filtered off, dried under *vacuo* over anhydrous calcium chloride.

Characterization

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

Reaction mechanism

Table 1 shows the color, physical characteristic, micro-analytical data and molar conductance measurements of Cu(II), Zn(II), Ag(I), Cd(II), Hg(II)-urea complexes. The elemental analysis data the prepared complexes revealed 1:1 molar ratio (M:U) for all complexes are in a good agreement with the general formulas $CuCl_2.2U.CH_3OH.\ 4H_2O$ (**1**), $ZnCl_2.U.\ CH_3OH\ .4H_2O$ (**2**), $AgNO_3.U.CH_3OH.6H_2O$ (**3**) $CdCl_2.U.CH_3OH.4H_2O$ (**4**) $HgCl_2.U.CH_3OH.6H_2O$ (**5**). The reactions can be represented by the stoichiometric equations:

$CuCl_2.2H_2O + 2U + CH_3OH \xrightarrow{25^{o}\,C} CuCl_2.U.CH_3OH.4H_2O$ (**1**)

$ZnCl_2 + 2U + CH_3OH \xrightarrow{25^{o}\,C} ZnCl_2.U.CH_3OH\ .4H_2O$ (**2**)

$AgNO_3 + 2U + CH_3OH \xrightarrow{25^{o}\,C} AgNO_3.U.CH_3OH.6H_2O$ (**3**)

$CdCl_2 + 2U + CH_3OH \xrightarrow{60^{o}\,C} CdCl_2.U.CH_3OH.4H_2O$ (**4**)

$HgCl_2 + 2U + CH_3OH \xrightarrow{25^{o}\,C} HgCl_2.U.CH_3OH.6H_2O$ (**5**)

The complexes are air-stable, hygroscopic, with low melting points, soluble in H_2O and dimethylsulfoxide, DMSO. The molar conductivities of the complex solution prepared in DMSO (10^{-3} g/5mL) (Table 1) indicates 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) Ω^{-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^- or NO_3^- ions are precipitated with colored solution by adding of $AgNO_3$ or $FeSO_4$ solutions, respectively, this experimental test is a good matched with CHN data. All these complexes have electrolytic properties. This fact elucidated that the Cl^- or NO_3^- are present. These results establish the stoichiometries of these complexes, which are in agreement with the general formulas, were suggested. The UV-visible spectra of the urea complexes are given in Table 2, which show the absorption bands of the metal ions toward urea.

Magnetic measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance according to the Gauy method. The calculations were evaluated by applying the following equations:

$$\chi_g = \frac{cl(R - R_o)}{10^9 M}$$

$$\chi_m = \chi_g MWt.$$

$$\mu_{eff} = 2.828\sqrt{\chi_m T}$$

where χ is mass susceptibility per gm sample

c is the calibration constant of the instrument and equal to 0.0816

R is the balance reading for the sample and tube

R_o is the balance reading for the empty tube

M is the weight of the sample in gm

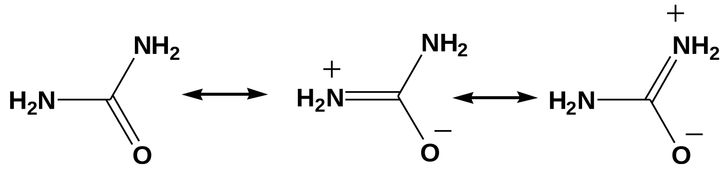
T is the absolute temperature

The magnetic moments of the $CuCl_2.U.CH_3OH.4H_2O$ (**1**) complex at T= 300 K and their corresponding hybrid orbitals were calculated. The observed values of the effective magnetic moments μ_{eff} measured for the complex was 1.81 B.M., this is in convenient with experimental value of 1.85 B.M. obtained for planar Cu(II) complex with dsp^2 hyperdization [42].

IR spectra

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. The band locations were measured for the mentioned urea complexes, together with the proposed assignments for the most characteristic vibrations are presented in Tables 3 and 4. In order to facilitate the spectroscopic analysis and to put our hand on proper structure of the prepared complexes, the spectra of the urea complexes were accurately compared with those of the urea and similar complexes in literature survey. The assignments of full vibrational analysis of crystalline urea have been published [38]. 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, U [38] and its $[Pt(urea)_2Cl_2]$ and $[Cr(urea)_6]Cl_3$ complexes [38]. The effect of the coordination on the spectra of the complexes of urea with $[Pt(urea)_2Cl_2]$ and

$[Cr(urea)_6]Cl_3$ 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 $[Pt(urea)_2Cl_2]$ coordinate to the nitrogen, whereas Fe(III), Zn(II), and Cu(II) coordinate to the oxygen of urea [38]. The distinguished bands of *v*(C–N) are exhibited at lower wavenumbers in the spectra of $AgNO_3.U.CH_3OH.6H_2O$ (**3**) complex than for free urea, whereas the *v*(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 +N=C–O− resonance features [43], see Scheme 3.



Scheme 3: Resonance types of urea

Concerning, $CuCl_2.U.CH_3OH.\ 4H_2O$ (**1**), $ZnCl_2.U.\ CH_3OH\ .4H_2O$ (**2**), $CdCl_2.\ U.\ CH_3OH.4H_2O$ (**4**)$HgCl_2.\ U.\ CH_3OH\ .6H_2O$ (**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 [43, 44]. The one IR-active *v*(M–O) vibration of Cr(III), Cd(II) and Zn(II) urea complexes presence at 442, 473, and 443 cm^{-1} [43, 44]. The band related to the stretching vibration ν(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, $\delta(H_2O)$, 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 nitrato group, NO_3^-, is observed at around (1385 and 1160 cm^{-1} attributed to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively [46]. The stretching motion of (ν(N=O)) is observed at 1475 cm^{-1} as a strong band, while the bending motion of the type $\delta(NO_2)$ are well resolved and observed at 786 as a medium band.

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

Complexes Empirical formula (MW.)	Color	Molar ratio	Elemental analysis (%), Found (Calcd.)		
			C	H	N
$CuCl_2.U.Me.4H_2O$ (**1**) 298.48 g/mol	Green	1:1	08.36 (08.04)	04.83 (05.36)	09.14 (09.36)
$ZnCl_2.\ U.Me.4H_2O$ (**2**) 300.29 g/mol	White	1:1	08.19 (07.99)	04.66 (05.33)	9.88 (09.32)
$AgNO_3.U.Me.6H_2O$ (**3**) 369.87 g/mol	White	1:1	06.51 (06.49)	04.83 (05.41)	08.31 (07.57)
$CdCl_2.\ U.Me.4H_2O$ (**4**) 347.32 g/mol	White	1:1	07.27 (06.91)	04.31 (04.61)	08.19 (08.06)
$HgCl_2.U.4Me.6H_2O$ (**5**) 471.50 g/mol	White	1:1	05.25 (05.09)	04.09 (04.24)	05.33 (05.94)

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

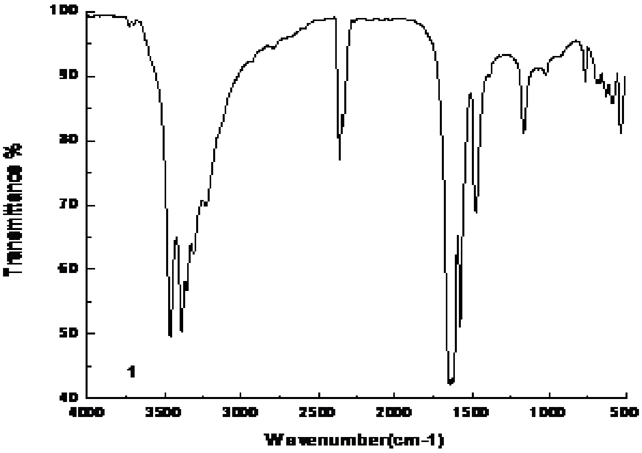
Complex	Λm, ($\Omega^{-1}cm^2mol^{-1}$)	μ_{eff}	Electronic transition	
			Bands	Assignments
$CuCl_2$.U.Me.4H_2O (**1**)	80	1.81	233 294	n—π* π—π*
$ZnCl_2$. U.Me.4H_2O (**2**)	25	-	230	π—π*
$AgNO_3$.U.Me.6H_2O (**3**)	334	-	232	π—π*
$CdCl_2$. U.Me.4H_2O (**4**)	57	-	235	π—π*
$HgCl_2$.U.4Me.6H_2O (**5**)	19	-	238	π—π*

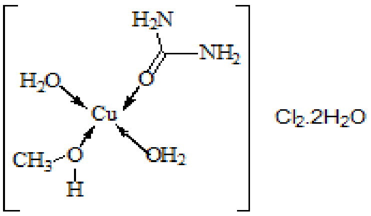
Table 3: Characteristic infrared frequencies (cm^{-1}) and tentative assignments of urea (U), [Pt(urea)$_2$Cl$_2$] (A), [Cr(urea)$_6$]Cl$_3$ (B), $CuCl_2$.U.Me.4H_2O (1) , $ZnCl_2$.U.Me.4H_2O (2) and $AgNO_3$.U.Me.6H_2O(3) complexes.

U	A	B	1	2	3	Assignments[(b)]
3450	3390 3290	3440 3330	3461 3388	3466 3352	3440 3346	ν_{as} (NH_2) ν(OH);CH_3OH
3350	3130 3030	3190	2361	3256	3205	νs(NH_2) ν (CH_3);CH_3OH
1683	1725	1505	1622	1640	1679	δ(C=O)
1471	1395	1505	1471	1489	1383	ν(C–N)

Table 4: Characteristic infrared frequencies (cm^{-1}) and tentative assignments of urea (U), [Pt(urea)$_2$Cl$_2$] (A), [Cr(urea)$_6$]Cl$_3$ (B), $CdCl_2$. U.Me.4H_2O (4) and $HgCl_2$.U.4Me.6H_2O (5)complexes

U	A	B	4	5	Assignments[(b)]
3450	3390 3290	3440 3330	3481 3418	3462 3356	ν_{as} (NH_2) ν(OH);CH_3OH
3350	3130 3030	3190	3369 3208	3814	νs(NH_2) ν (CH_3);CH_3OH
1683	1725	1505	1628	1613	δ(H_2O) δ(C=O)
1471	1395	1505	1581	1446	ν(C–N)





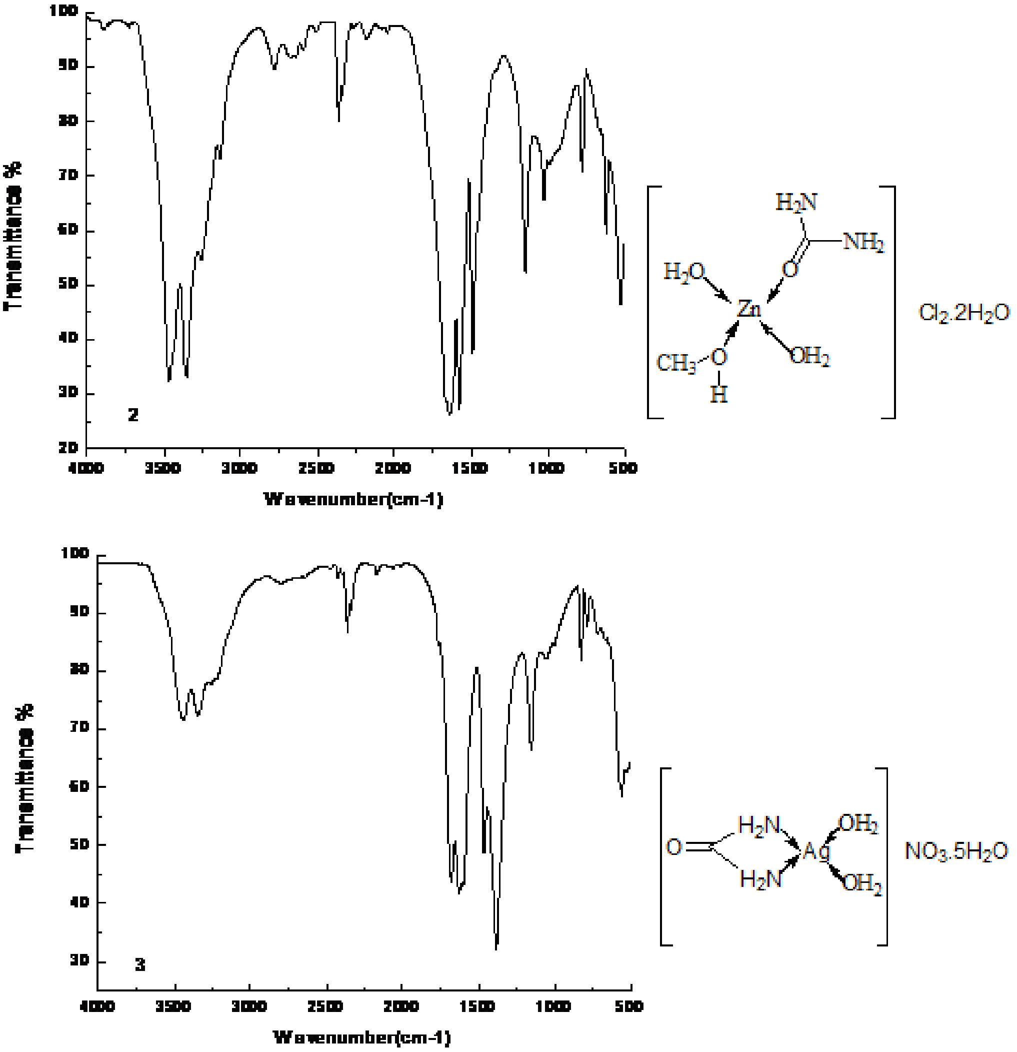
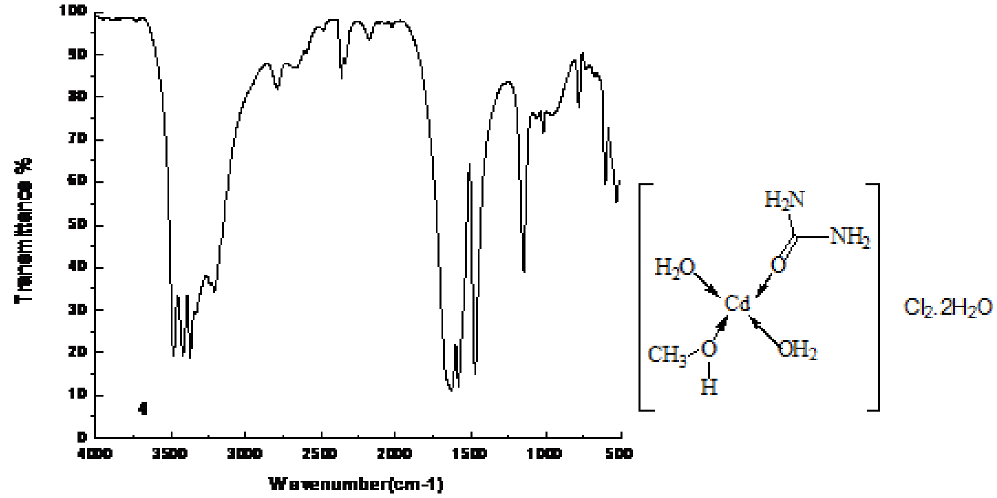


Fig. 1: Infrared spectra of urea complex at room temperature: $CuCl_2$.U.Me.4H_2O (1), $ZnCl_2$.U.Me.4H_2O (2), $AgNO_3$.U.Me.6H_2O (3), $CdCl_2$.U.Me.4H_2O (4), $HgCl_2$.U.4Me .6H_2O (5)



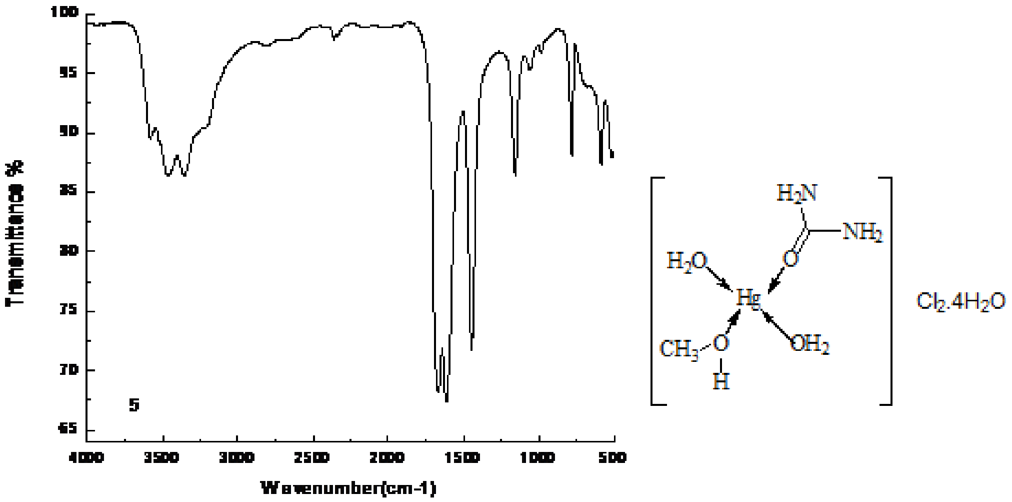


Fig. 1: (*Continued*).

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