



COMPLEXES OF UREA WITH ALUMINUM (III) CHLORIDE AND ACETATE

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ABSTRACT

The chelation of urea (U) with aluminum ion at 90°C were studied by elemental analyses and infrared spectroscopy. The elemental analyses and spectral data were well explained in terms of the formation of $\text{AlCl}_3 \cdot \text{U} \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (1) and $\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2) complexes. 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 complexes formed between the metal ions and urea were distinguished.

Key words: Urea, Aluminum, 90°C, Elemental analyses, Infrared spectroscopy.

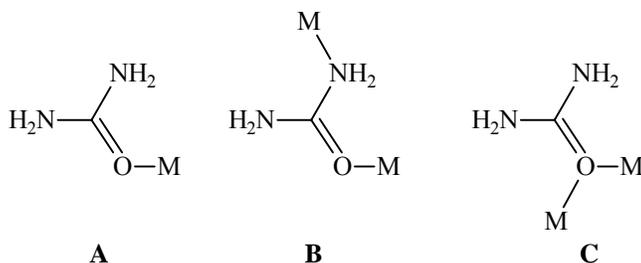
INTRODUCTION

Carbamide, carbonyldiamide or the most famous name, urea ($\text{CH}_4\text{N}_2\text{O}$) is a white solid, which melts at 132°C, soluble in water and ethanol was first prepared by Wöhler¹ 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. Urea may be prepared in the laboratory by the action of ammonia with carbonyl chloride, alkyl carbonates, chloroformates or urethans. Industrially²⁻⁴, urea is also 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. Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Adults excrete about 30 g 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, $\text{CO}(\text{NH}_2)_2 \cdot \text{HNO}_3$. Urea is used in industry in preparation of formaldehyde-Urea resin(plastics)⁵, barbiturates⁶, fertilizers⁷⁻¹⁰, in the paper industry to soften cellulose and has

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been used to promote healing in infected wounds and many other applications in the field of medicine¹¹⁻²².

Crystal structure studies have shown that in solid urea, both nitrogen atoms are identical. Bond length measurements⁶ in urea give the C-N distance as 1.37 Å, while, in aliphatic amines the C-N bond length is 1.47 Å. 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...M angle considerably smaller than 180°, in accordance with the sp^2 hybridization of the O atom (**A** in **Scheme 1**). The rare N,O-bidentate coordination mode (**B** in **Scheme 1**) 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 atom²⁵ (**Scheme 1**).



Scheme 1: The coordination modes of urea towards metal ions

Raman and infrared spectra of urea have been observed by several investigators²⁷⁻³². The normal vibrations of the urea molecule were calculated by Kellner and others³³⁻³⁶ based on the result of these calculations, Yamaguchi et al.³⁶, assigned all the observed frequencies in the spectra of urea to the vibrations of the frequencies 1686 and 1603 cm^{-1} due to CO stretching and NH_2 bending motions, whereas Stewart³⁷ assigned the 1686 cm^{-1} band to CO stretching vibration and the 1603 cm^{-1} band to NH_2 bending motion. The calculations studied by Yamaguchi showed that for the band at 1686 cm^{-1} , the contribution of the NH_2 bending motion is greater than that of CO stretching motion. The 1464 cm^{-1} frequency of urea is assigned to the CN stretching vibration. The 1150 cm^{-1} band is assigned to NH_2 rocking vibrations of 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-C** 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 completely³⁶, 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, respectively³⁸. 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 urea³⁸. 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} .³⁹ Recently, urea represents not only an important molecule in biology⁴⁰ but also an important raw material in chemical industry⁴¹. The aim of this publication is to report the synthesis, characterization, of the resulting compounds formed from the reactions of urea with AlCl_3 , and $\text{Al}(\text{CH}_3\text{COO})_3$ at 90°C .

EXPERIMENTAL

Materials

Urea, AlCl_3 , $\text{Al}(\text{CH}_3\text{COO})_3$ 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.

Synthesis of urea complexes

The complexes, $\text{AlCl}_3 \cdot \text{U} \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (**1**) and $\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (**2**) were prepared by mixing equal methanolic solutions of AlCl_3 (1.33 g, 0.01 mole), $\text{Al}(\text{CH}_3\text{COO})_3$ (2.04 g, 0.01 mol), 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 amount of the formed precipitate increased with standing time. The complexes formed were filtered off, dried under *vacuo* over anhydrous calcium chloride.

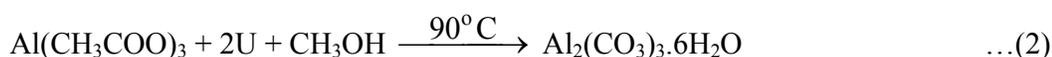
Measurements

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 infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer (4000-400 cm^{-1}).

RESULTS AND DISCUSSION

The color, physical characteristic, micro-analytical data, of aluminum complexes are given in Table 1. The elemental analysis data of the prepared complexes revealed 1:1 molar ratio (M:U) for complex (1) only are in a good agreement with the general formulas $\text{AlCl}_3 \cdot \text{U} \cdot 2\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ (1) and $\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2) The reactions can be represented by the stoichiometric equations:



The complexes are air-stable, hygroscopic, with low melting points, soluble in H_2O .

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

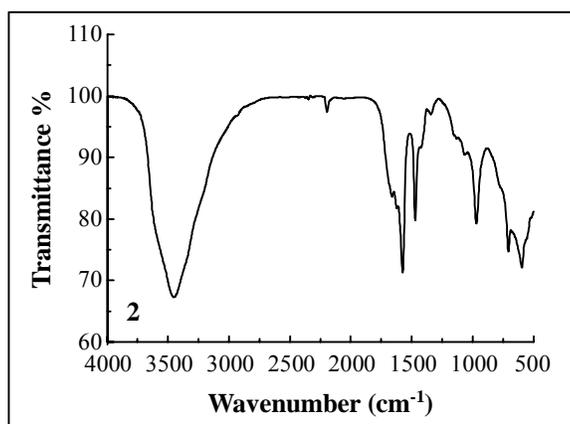
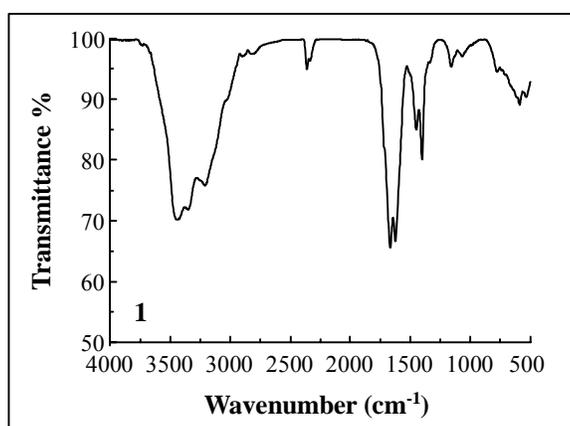
Complexes Molecular formula Empirical formula (MW.)	Color	Molar ratio	Elemental analysis (%) Found (Calcd.)		
			C	H	N
$\text{AlCl}_3 \cdot \text{U} \cdot 2\text{Me} \cdot \text{H}_2\text{O}$ (1) 275.34 g/mol	White	1:2	13.30 (13.07)	06.08 (05.08)	08.23 (10.17)
$\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2) 341.96 g/mol	White	1:2	10.01 (10.53)	00.00 (0000)	03.39 (03.59)

Infrared spectra

The infrared spectra of the aluminum and urea complexes are shown in Figs. 1 & 2, respectively. The band locations were measured for the mentioned 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 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 published³⁸.

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), $\text{AlCl}_3 \cdot \text{U} \cdot 2\text{Me} \cdot \text{H}_2\text{O}$ (1) and $\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2)

U	A	B	1	2	Assignments
3450	3390	3440	3442	-	$\nu_{\text{as}}(\text{NH}_2)$
	3290	3330	3350	-	$\nu(\text{OH}); \text{CH}_3\text{OH}$
3350	3130	3190	3210	-	$\nu_{\text{s}}(\text{NH}_2)$
	3030				$\nu(\text{CH}_3); \text{CH}_3\text{OH}$
1683	1725	1505	1625	1623	$\delta(\text{C}=\text{O})$
1471	1395	1505	1403	-	$\nu(\text{C}-\text{N})$



Figs. 1 & 2: Infrared spectra of complexes: $\text{AlCl}_3 \cdot \text{U} \cdot 2\text{Me} \cdot \text{H}_2\text{O}$ (1) and $\text{Al}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ (2)

Table 2 gives diagnostic infrared peaks of the free urea ligand, published work and aluminum 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 $[Cr(urea)_6]Cl_3$ complexes³⁸. 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, respectively³⁸. 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 urea³⁸. Concerning, $AlCl_3.U.2CH_3OH.H_2O$ complex, the coordination mode takes 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^{52,53}. The one IR-active $\nu(M-O)$ vibration of complex (1) is shown at 405 cm^{-1} .⁵²⁻⁵⁵ The band related to the stretching vibration $\nu(O-H)$ of uncoordinated H_2O is observed as expected in the range of $(3442-3452)\text{ cm}^{-1}$, while the corresponding bending motion of the uncoordinated water, $\delta(H_2O)$, is observed in the range of $(1623-1625)\text{ cm}^{-1}$. For $Al_2(CO_3)_3.6H_2O$ (2) the band related to the carbonates is shown at 1473 cm^{-1} .

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