



Complexes of urea with Mn(II), Fe(II) Metal ions and synthesis of Mn(II), Fe(II) complexes

Pooja Singh Gautam

Department of Chemistry, Sitaram Samarpan Mahavidhyalaya, Naraini, Uttar Pradesh, India

Abstract

The complexation of urea (U) with Mn(II), Fe(II) ions at different temperatures has been studied by many methods namely elemental analysis, magnetic susceptibility, conductivity measurement. The solubility tests of the complexes were carried out, in which Mn(II) complex was found to be soluble in water and Fe(II) complex was found to be slightly soluble in water. The physical and spectral data were well explained in terms of the formation of $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 3\text{U} \cdot 5\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 3\text{U} \cdot 3\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 6\text{U}$ complexes of urea and synthesized at room temperature and 60°C respectively. On the basis of the infrared spectra data and the values of stretching vibrational band of both C=O and NH_2 groups, the complexation of metal ions toward urea was distinguished.

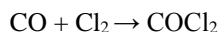
Keywords: transition metals, urea, biological activity, infrared spectra, thermal analysis

Introduction

Urea may be prepared in the laboratory by 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 the formed ammonium carbamate at $130\text{--}150^\circ\text{C}$ under. About 35 atmospheric pressure. The carbamate is decomposed to form urea and water according to the following reaction.

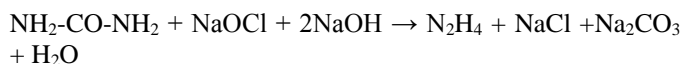


Conversion of CO to urea



Carbonyl chloride (phosgene)

Urea is used for the manufacture of hydrazine in which urea is treated with alkaline sodium hypochloride e.g-



Urea possesses two types of potential donor atoms. the carbonyl oxygen and amide nitrogen. Penl and *et al.* studied the infrared spectra of urea complexes to determine, whether co-ordination occurs through oxygen or nitrogen atoms. The electronic structure of urea may be represented by a resonance hybrid of structure. If co-ordination occurs through nitrogen, contributions of structure 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 1700 cm^{-1} (39). Urea represents not only an important molecule in biology but

also an important raw material in chemical industry.

Materials

Urea $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, MnCl_2 and methanol solvent were obtained from Aldrich company. All chemicals used in this study were of analytical grade and they were used without further purification.

Synthesis of urea complexes at room temperature

The complexes, $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$, and $\text{MnCl}_2 \cdot 3\text{U} \cdot 3\text{H}_2\text{O}$. Were prepared by mixing equal methanolic solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.70, 0.01 mole) or MnCl_2 (1.98, 0.01 mole) in methanol with 50 ml volume of urea solution (2.40g, .04 mole) in methanol solvent. The mixtures were stirred for about 2 hours then heated to 60°C for 6 hours on a water bath under refluxed system, the precipitated products were filtered, dried system, the precipitated products were filtered, dried at 60°C in on oven for 3 hours.

Synthesis of urea complexes at 70°C temperature.

The urea complexes $\text{FeCl}_2 \cdot 3\text{NH}_2\text{CONH}_2 \cdot 3\text{H}_2\text{O}$. and $\text{MnCl}_2 \cdot 6\text{NH}_2\text{CONH}_2$. Were prepared by a method similar to that described for the preparation of urea complexes at room temperature. 25 ml volume of urea solution (2.4g, 04 mole) was mixed with an equal volume of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.70g, 0.01mole) or MnCl_2 (1.98g, 0.01mole) 25 ml methanol. The mixtures were stirred for about 2 hours then heated to 60°C for 6 hour on a water both under refluxed system. The precipitated products were filtered. Dried at 60°C in an oven for 3 hours.

Physical Measurement

Metal ion analysis was carry out by the dissolution of solid complex in hot concentrated nitric acid. Further diluting with distilled water and filtered to remove the precipitated organic ligands. Remaining solution was neutralized with ammonia solution and the metal ions were litrated against urea.

The many media available, National committee for clinical laboratory standards (NCCLS) recommend Mueller- Hinton agar due to. It results in good batch to – batch reproducibility. Disc diffusion method for filamentous fungi tested by using approved standard method (M38) developed by the NCCLS for evaluating. The susceptibility of filamentous funge to antifungal agents. Disc diffusion method for yeast developed standard method (M44.P) by the NCCLS [47]. Plates in oculated with filamentous fungi as aspergillus flavus at 25°C foe 48 hours. Gram (+) bacteria as staphylococcus Aureus. Bacillus subtilis Gram (-) bacteria as Escherichia coli, pseudomonas aeruginosa they were incubated at 35-37°C for

24-48 hours and yeast as candida albicans incubated at 30°C for 24-48 hours and, then the diameters in millimeters [42]. Standard discs of tetracycline (Anti-bacterial agent). Amphotericin (Anti-fungal agent) served as positive controls for antimicrobial activity but filter disc impregnated with 10ul of solvent (distilled water. Chloroform, DMSO) were used as a negative control.

Result and Discussion

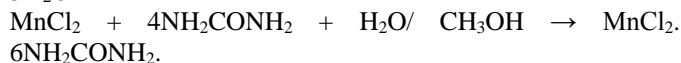
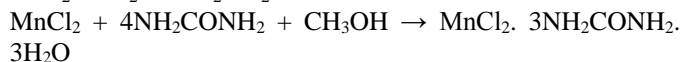
The colour, physical characters micro analytical data, molar conductance measurements of Fe(II) and Mn(II) urea compound given table.

Table 1: Physical characterization, microanalytical data of urea complexes.

Complexes molecular formula. Empirical formula (mw).	Color	Molar ratio	Elemental analysis (%)	
			Found (calc)	
			C	H
FeCl ₂ . 6U.3H ₂ O 540.8g/mol	Yellow	1:4	12.40	0.240
FeCl ₂ .3U.5H ₂ O 396.8g/mol	Brown	1:4	08.84	04.70
MnCl ₂ .3U.3H ₂ O 431.91g/mol	White creamy	1:4	0.750	04.30
MnCl ₂ .6U 557.91g/mol	White	1:4	11.70	04.60

The elemental analysis data of some prepared complexes revealed 1:4 molar ratio (M:U).

(M = Mn (II), Fe (II) and U= urea) are in a good agreement with the general formulas FeCl₂. 6U.3H₂O.and MnCl₂.3U.3H₂O on one hand FeCl₃.3U.5H₂O and MnCl₂.6U. complexes on the other hand. Prepared at room temperature and 60°C respectively. The reaction can be represented by the stoichiometric equations.



Complexes are air- stable, hygroscopic, with low melting point, soluble in H₂O dimethy formamide DMF. The molar conductivities of (0.01g per 5ml) the prepared complexes in DMF. Indicate that the complexes have an electrolytic nature.

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

Complex	$\Omega\text{Cm}^2 \text{ mole}^{-1}$	μ_{eff}
FeCl ₂ . 6U.3H ₂ O	946	2.95
FeCl ₂ .3U.5H ₂ O		2.91
MnCl ₂ .3U.3H ₂ O	95	2.73
MnCl ₂ .6U		6.17

Infrared spectra

The infrared spectra of the Fe(II) and Mn(II) urea complexes at room temperature and 60°C temperature. The band

locations were measured for the mentioned urea complexes, together with the proposed assignments for the most characteristic vibrations are presented in table.

Table 3: Characteristic infrared frequencies (Cm-1) and tentative assignments of urea (U).

U	A	B	1	2	Assignments (b)
3450	3390 3290	3440 3330	3464 3354	3437 3350	V(OH); H ₂ O V _{as} (NH ₂)
3350	3130 3030	3190	3219	-	V _s (NH ₂)
1683	1725	1505	1658	1656	δ (C=O) δ (H ₂ O)
1471	1395	1505	1496	1473	V(C- N)

[Pt(urea)₂Cl₂] (A), [Cr(urea)₆]Cl₃ (B),
MnCl₂. 3NH₂CONH₂.3H₂O and MnCl₂.6NH₂CONH₂. two complexes.

Table 4: Characteristic infrared frequencies (Cm⁻¹) and tentative assignments of urea (U),

U	A	B	1	2	Assignments (b)
3450	3390 3290	3440 3330	3450 3346	3448 3358	V(OH); H ₂ O V _{as} (NH ₂)
3350	3130 3030	3190	3202	3198	V _s (NH ₂)
1471	1725	1505	1630	1630	δ (c=O)
1471	1395	1505	1495	1402	V(C- N)

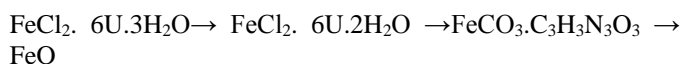
[Pt(urea)₂Cl₂] (A), [Cr(urea)₆]Cl₃ (B),
FeCl₂.6NH₂CONH₂.3H₂O and FeCl₂. NH₂CONH₂. H₂O complexes.

Thermal Analysis

The FeCl₂.6U. 3H₂O. and FeCl₂. 3U.5H₂O. MnCl₂. 3U.3H₂O and MnCl₂.6U complexes were studied by thermogravimetric analysis from ambient temperature to 80°C in oxygen

atmosphere. TG curve and decomposition stages obtained for these complexes with a temperature rate 30°C/min. The TG-DTG cure of $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$ complex four stages of transitions are observation in the TG- DTG curve. The first transition changes from 42°C to 159°C with DTG max = 54°C, with an experimental mass loss of 4.134% against a theoretical loss of 3.328% corresponding to the release of 1 mole of water.

The second transition changes from 15°C to 290°C with DTG max= 243°C, with an experimental mass loss of 45.382% against a theoretical loss of 46.9708 corresponding to the release of 2 mole water, 2 mole of ammonium chloride, 3 mole of ammonia, 1 mole of hydrazine and 1 mole of N_2 . The third transition is from 290°C to 397°C with DTG_{max} =351°C and an experimental mass lose of 32.033% against a theoretical loss of 32.00%, corresponding to the release of 1 mole cyanuric acid and 1 mole carbon dioxide. In the final transition 1 mole carbon monoxide is released this take place between 397°C and 642°C with DTG_{max} at 417°C. The thermal decomposition of the above complex can represented.



The TG cure for $\text{MnCl}_2 \cdot 3\text{U} \cdot 3\text{H}_2\text{O}$ complex has three stages of mass losses within the temperature range 156- 624°C at 267, 387 and 480°C DTG maximum peaks. The first stage is between 156-325°C an with experimental mass loss of 39.858 against a theoretical mass loss of 40.286%, corresponding to the loss of 3 moles water and 1 mole of urea. The second stage is between 325-432°C with an experimental and theoretical mass losses of 11.92% and 12.387% respectively, is due to the loss of ammonium chloride.

The third stage of decomposition at temperature rang 432-624°C is assigned to the loss of half Cl_2 and 1 CN with an experimental mass loss of 13.538% and a theoretical mass loss of 14.239% leaving MnO_2 as a result of trapping half O_2 from air.

The proposed thermal decomposition mechanism of the complex can given as.

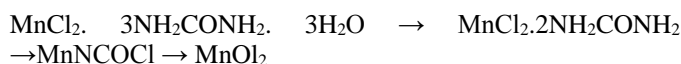


Table 5: The maximum temperature, $T_{\text{max}}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$, and $\text{FeCl}_2 \cdot 3\text{U} \cdot 5\text{H}_2\text{O}$ complexes

Complexes	Decompositions	$T_{\text{max}}/^\circ\text{C}$	Lost species	% Weight Found	Loss Calc.
$\text{FeCl}_2 \cdot 6\text{U} \cdot 3\text{H}_2\text{O}$	First step	6.4	H_2O	4.135	3.328
	Second step	243	$2\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} + 3\text{NH}_3 + \text{N}_2 + \text{H}_4 + \text{N}_2$	45.382	46.970
	Third step	351	$\text{C}_3\text{H}_3\text{N}_3\text{O}_3 + \text{CO}_2$	32.00	32.033
	Forth step	417	CO	3.600	5.180
	residue		FeO	13.314	12.489
$\text{FeCl}_2 \cdot 3\text{U} \cdot 5\text{H}_2\text{O}$	First step		$\frac{1}{2}\text{H}_2\text{O}$	6.856	6.804
	Second step	238	$3.5\text{H}_2\text{O} + 2\text{urea}$	46.491	46.119
	Third step	370	$\text{HCN} + 2\text{HCl} + \frac{1}{2}\text{N}_2 + \frac{1}{2}\text{H}_2$	27.955	28.981
	residue		FeO	18.145	18.096

Table 6: The maximum temperature, $T_{\text{max}}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $\text{MnCl}_2 \cdot 3\text{U} \cdot 3\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 6\text{U}$ complexes.

Complexes	Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost species	% Weight Found	Loss Calc.
$\text{MnCl}_2 \cdot 3\text{U} \cdot 3\text{H}_2\text{O}$	First step	267	$4\text{NH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$	39.585	40.286
	Second step	387	NH_4Cl	11.929	12.387
	Third step	480	$\frac{1}{2}\text{Cl}_2 + \text{CN}$	13.533	14.239
	Residue		MnO_2	20.129	-
$\text{MnCl}_2 \cdot 6\text{U}$	First step	260	$7\text{NH}_3 + 3\text{CO}_2 + \text{N}_2$	41.276	41.405
	Second step	466	$\text{C}_2\text{H}_3\text{N}_3\text{O}_3$	20.778	20.98
	residue	-	$\text{MnCl}_2 + \text{carbon}$	22.573	-

Biological Evolution

Biological evaluations were checked in term of antimicrobial activities of torget compound against gram- positive and gram-negative and to strains of fungus.

Eg- *Bacillius subtilis* and *staphylococcus aureus*, *Escherichia coli* and *pseudomonas aeruinos*a, *aspergillus flavus* and *candida albicans*. All complexes were found to be efficient antimicrobial agents except for complexes- which has no efficiency against *staphylococcus aureus*, *aspergillus flavus* and *candida albicans* fungus.

Conclusion

The complexes were formed in 1:2 (Metal-ligand) ratio as

confirmed by the microanalysis. The molar conductivity data of the complexes in methanol KI indicator that they are non-electrolytes. All the complexes are air stable and soluble inpratic solvents like methanol and ethanol. The in vitro antimicrobial study shows that the complexes have higher activities compared to the free ligand.

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