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Chromium (III), Manganese (II), Cobalt (II), Iron (III) and Nickel (II) Complexes with Urea at High Temperature: Preparation and Spectroscopic Studies.

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ABSTRACT

The aim of this work is to report the synthesis, characterization, conductance and spectroscopic studies of the resulting complexes formed from the reactions of urea (U) with $CrCl_3.6H_2O$, $MnCl_2$, $FeCl_3.6H_2O$, $Co(NO_3)_2.6H_2O$, and $Ni(NO_3)_2.6H_2O$ at temperature of 90 °C. The obtained complexes were characterized using elemental analysis, magnetic susceptibility, conductivity measurement, UV-visible and infrared spectroscopy. The elemental, physical and spectral data indicates the formation of $CrCl_3.U.Me.10H_2O$, $MnCl_2.U.Me$, $FeCl_3.U.Me.6H_2O$, $Co(NO_3)_2.U.Me.14H_2O$ and $Ni(NO_3)_2.U.5Me$ complexes. Based on the values of ν(C=O) and ν(N-H) groups, the complex formation of these metal ions with urea was distinguished.

Keywords: Urea, Transition metals, High temperature, Conductivity, IR spectra.

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INTRODUCTION

Complexes of urea with some metal ions are used as fertilizers [1-4]. Its complexes with zinc sulphate and nitrate have very important application in this field [5]. These two complexes were found to increase the yield of rice more than a dry mixture of urea-zinc salt does. Calcium nitrate-urea complex, $[Ca(urea)_4](NO_3)_2$, [6,7] 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 [8]. Urea possesses two types of potential donor atoms, the carbonyl oxygen and the two amide nitrogen. The IR spectra of urea complexes were extensively studied in order to determine whether coordination occurs through oxygen or nitrogen atoms. If coordination occurs through nitrogen, this results in an increase of the CO stretching frequency with a decrease of CN stretching frequency while N-H stretching frequency fall to the same range as those of the amido complexes. If coordination occurs through oxygen 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 [9], 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 [10]. 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 [10]. 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 1700 cm^{-1} [11]. Recently, urea represents not only an important molecule in biology [12] but also an important raw material in chemical industry [13]. Herein, in this paper, the complexes of urea with $CrCl_3.6H_2O$, $MnCl_2$, $FeCl_3.6H_2O$, $Co(NO_3)_2.6\ H_2O$, and $Ni(NO_3)_2.6H_2O$ at high temperature were reported.

EXPERIMENTAL

General

Urea, $CrCl_3.6H_2O$, $MnCl_2$, $FeCl_3.6H_2O$, $Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, and methanol were obtained from Aldrich Company. Urea was received from Fluka chemical company. All chemicals used in this study were of analytical grade and they were used without further purification. The elemental analysis 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/5cm^3 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.

Synthesis

Complexes of $CrCl_3$.U.Me.$10H_2O$ (**1**), $MnCl_2$.U.Me.(**2**) $FeCl_3$.U.Me.$6H_2O$ (**3**), $Co(NO_3)_2$.U.Me.$14H_2O$ (**4**), and $Ni(NO_3)_2$.U.5Me (**5**) were prepared by mixing equal solutions of $CrCl_3.6H_2O$ (2.66 g, 0.01 mole), $MnCl_2$ (1.98 g, 0.01 mole), $FeCl_3.6H_2O$ (2.70 g, 0.01 mole), $Co(NO_3)_2.6H_2O$ (2.91 g, 0.01 mole), and $Ni(NO_3)_2.6H_2O$(2.91 g, 0.01 mole) in 25 mL methanol with a 50 mL volume of urea solution (1.20 g,.02 mole) in methanol solvent. The mixtures were stirred for about 12 hours under refluxed system at 90 °C. In all cases, the amount of the formed precipitate increased with time. The precipitated colored complex formed in each case was filtered off, dried under *vacuo* over anhydrous calcium chloride.

RESULTS AND DISCUSSION

Reaction mechanism

The reactions of urea with the reported metal ions can be represented by the following equations:

$$CrCl_3.6H_2O + 2\,U + CH_3OH \xrightarrow{90^{O}C} CrCl_3.U.\,CH_3OH.10H_2O\ (\mathbf{1})$$

$$MnCl_2 + 2U + CH_3OH \xrightarrow{90^{O}C} MnCl_2.U.CH_3OH\ (\mathbf{2})$$

$$FeCl_3.6H_2O + 2\,U + CH_3OH \xrightarrow{90^{O}C} FeCl_3.U.CH_3OH.6H_2O\ (\mathbf{3})$$

$$Co(NO_3)_2.6H_2O + 2U + CH_3OH \xrightarrow{90^{O}C} Co(NO_3)_2.U.CH_3OH.14H_2O\ (\mathbf{4})$$

$$Ni(NO_3)_2.6H_2O + 2U + CH_3OH \xrightarrow{90^{O}C} Ni(NO_3)_2.U.5CH_3OH\ (\mathbf{5})$$

The color, physical characteristic, micro-analytical data, molar conductance measurements of Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and urea complexes are given in Table 1. The elemental analysis data of the prepared complexes revealed 1:1 molar ratio (M:U) for all the prepared complexes are in a good agreement with the general formulas $CrCl_3$.U. Me.$10H_2O$ (**1**), $MnCl_2$.U.Me (**2**) $FeCl_3$.U.Me.$6H_2O$ (**3**), $Co(NO_3)_2$.U.Me.$14H_2O$ (**4**), and $Ni(NO_3)_2$.U.5Me.(**5**) complexes.

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

Complexes Empirical formula (MW.)	Color	Molar ratio	Elemental analysis (%) Found (Calcd.)		
			C	H	N
$CrCl_3$.U.Me.$10H_2O$ (**1**) 430.55 g/mol	Green	1:2	05.55 (05.57)	06.00 (06.50)	05.54 (06.50)
$MnCl_2$. U. Me (**2**) 289.91 g/mol	Black	1:2	08.94 (08.28)	02.28 (02.76)	09.80 (09.66)
362.3 g/mol $FeCl_3$.U.Me.$6H_2O$ (**3**)	Brown	1:2	06.35 (06.62)	04.97 (05.52)	07.20 (07.73)
$Co(NO_3)_2$. U.Me.$14H_2O$ (**4**) 527.03 g/mol	Deep Pink	1:2	04.48 (04.55)	06.15 (06.07)	10.88 (10.62)
$Ni(NO_3)_2$.U.5Me (**5**) 402.85 g/mol	Pale Green	1:2	17.25 (17.87)	05.64 (05.96)	13.61 (13.90)

Conductivity and magnetic measurements

The molar conductivities of (0.003g per 5 ml) the prepared complexes in DMSO (Table 2) indicate that the complexes have an electrolytic nature. The molar conductivity values for the urea complexes in DMSO solvent are exhibited in the range of (55–144) Ω^{-1} cm^{2} mol^{-1}, suggesting them to be electrolytes (Table 2). 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.

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

Complex	Λm, (Ω^{-1}cm^{2}mol^{-1})	μ_{eff}	Electronic spectra	
			Bands	Assignments
$CrCl_3$.U.Me.10H_2O (**1**)	116	3.74	270 452 644	π—π* *n*—π* d—d, MLCT
$MnCl_2$.U.Me (**2**)	111	5.97	255	π—π*
$FeCl_3$.U.Me.6H_2O (**3**)	127	4.42	266 338	π—π* *n*—π*
$Co(NO_3)_2$.U.Me.14H_2O (**4**)	144	4.56	310 534	*n*—π* d—d, MLCT
$Ni(NO_3)_2$.U.5Me (**5**)	55	3.30	272 452 642	π—π* *n*—π* d—d, MLCT

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance according to the Gauy method. The magnetic moments of $CrCl_3$.U.CH_3OH.10H_2O (**1**) , $Ni(NO_3)_2$.U.5CH_3OH (**5**) and the other complexes at T= 300 K and their corresponding hybrid orbitals were calculated. The observed values of the effective magnetic moments μ_{eff} measured for the above complexes equal to 3.74 B.M and 3.30 B.M respectively this is convenient with experimental values for octahedral complexes due to sp^3d^2 hyperdization [14]. The UV-visible spectra of the urea complexes given in Fig. 1, and these bands were assigned in Table 2 within the range 260-1000 nm.

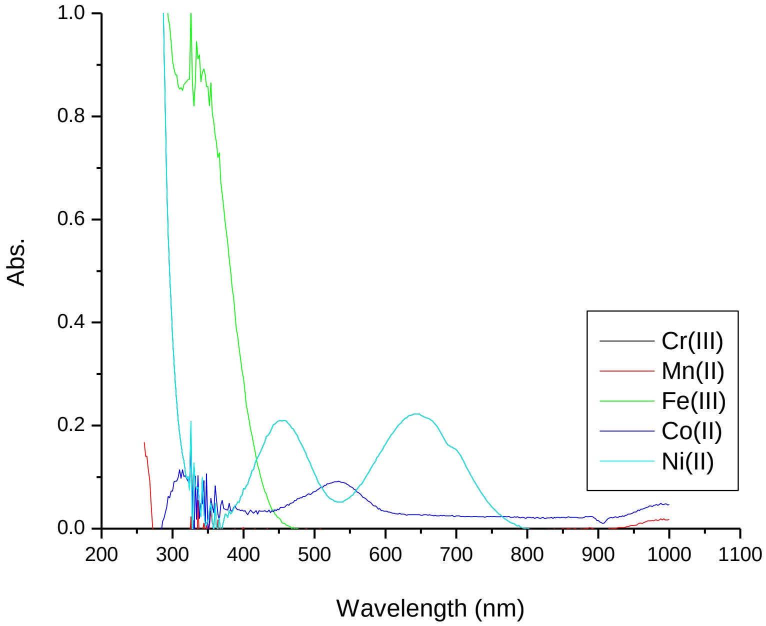


Fig. 1: UV-visible spectra of urea complex: $CrCl_3$.U. Me.$10H_2O$ (1), $MnCl_2$.U.Me (2), $FeCl_3$.U.Me.$6H_2O$ (3), $Co(NO_3)_2$.2U.Me.$14H_2O$ (4) and $Ni(NO_3)_2$.U.5Me (5)

Interpretation of the IR spectra

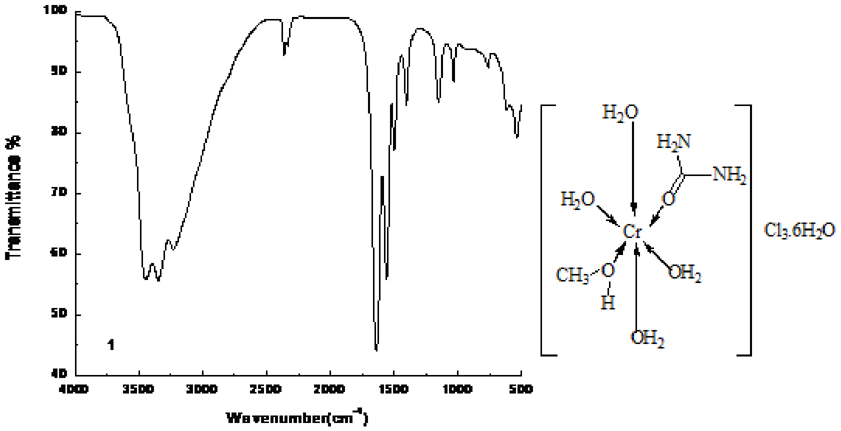
The infrared spectra of the Cr(III), Mn(II), Fe(III), Co(II), Ni(II) urea complexes at room temperature are shown in Fig. 2. The band locations were measured for the mentioned urea complexes, together with the proposed assignments for the most characteristic vibrations are presented in Tables 3 and 4. In order to facilitate the spectroscopic analysis and to put our hand on the 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. 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 [10]. Tables 3 and 4 give diagnostic infrared peaks of the free urea ligand, published work and Cr(III), Mn(II), Fe(II), Co(II) and Ni(II) complexes. Assignments have been given in comparison with the data obtained for the free urea, that is, uncoordinated urea and its $[Pt(urea)_2Cl_2]$ and $[Cr(urea)_6]Cl_3$ complexes [10]. 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. The mode of coordination of urea with metal ions seems to be dependent upon the type and nature of metal. Pt(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 [10]. For all the prepared complexes, 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 [15, 16]. The IR-active ν(M–O) vibration of all prepared urea complexes is observed at the range (556- 499) cm^{-1} [15, 16]. The band related to the stretching vibration ν(O-H) of uncoordinated H_2O is observed as expected in the range of (3440-3478) cm^{-1}, while the corresponding bending motion of the uncoordinated water, δ(H_2O), is observed in the range of (1637-1670) cm^{-1}. In both cobalt and nickel complexes, the characteristic stretching vibrations of the nitrate group, NO_3^-, is observed at around (1384 and 1156 cm^{-1} attributed to $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$, respectively [17, 18]. The stretching motion of (ν(N=O)) is observed at 1478 cm^{-1} and 1476 cm^{-1} as a strong band, while the bending motion of the type δ(NO_2) are well resolved and observed at 777 cm^{-1} and 785 cm^{-1} as a medium band.

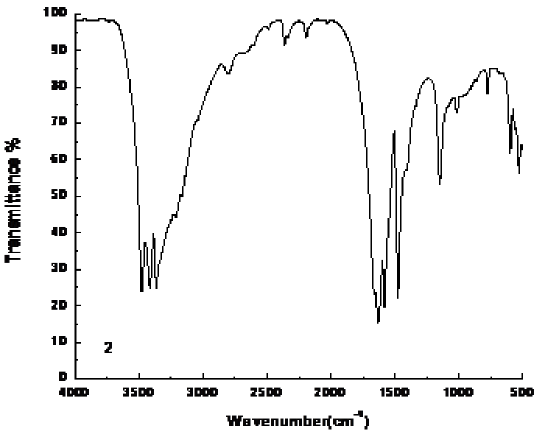
Table 3: Characteristic infrared frequencies (cm^{-1}) and tentative assignments of urea (U), [Pt(urea)$_2$Cl$_2$](A), [Cr(urea)$_6$]Cl$_3$(B), CrCl$_3$.U.8H$_2$O(1), MnCl$_2$.U.Me.(2) and FeCl$_3$.U.Me.6H$_2$O(3) complexes.

U	A	B	1	2	3	Assignments$^{(b)}$
3450	3390 3290	3440 3330	3440 3343	3478 3365	3467 3343	ν_{as} (NH_2) ν (OH); CH_3OH
3350	3130 3030	3190	2051	3162	3125	$\nu_s(NH_2)$
1683	1725	1505	1562	1587	1559	δ(C=O)
1471	1395	1505	1497	1477	1498	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), Co(NO$_3$)$_2$.U,Me.14H$_2$O(3) and Ni(NO$_3$)$_2$.U.5Me (4) complexes

U	A	B	4	5	Assignments$^{(b)}$
3450	3390 3290	3440 3330	- 3355	3439 3334	ν (OH); CH_3OH ν_{as} (NH_2)
3350	3130 3030	3190	2362	3212	$\nu_s(NH_2)$
1683	1725	1505	1588	1623	δ(H_2O) δ(C=O)
1471	1395	1505	1478	1467	ν (C–N)

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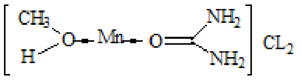
100
90
80
70
60
50
40
30
20
10
0
2
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber(cm⁻¹)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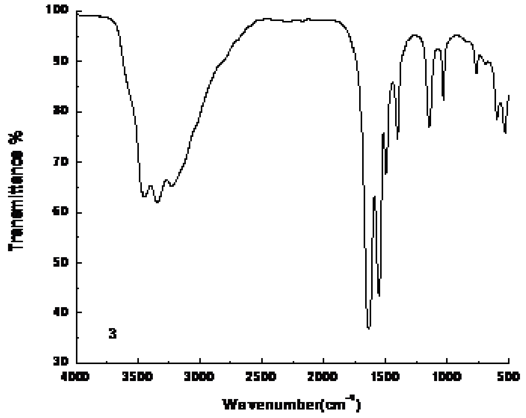
H
O
Mn
O
NH2
NH2
CL2


Transmittance %
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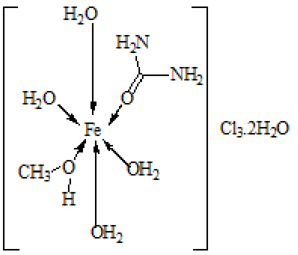
Wavenumber(cm⁻¹)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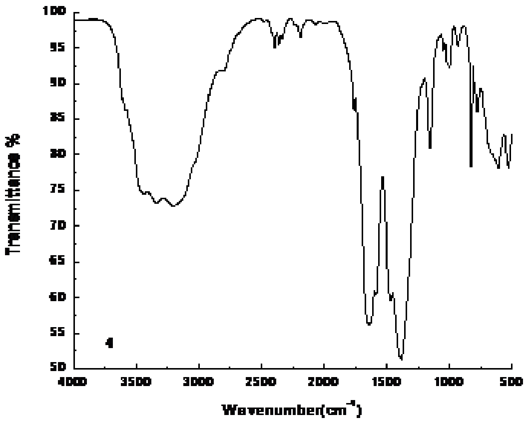
H2O
O
Fe
CH3
O
H
OH2
OH2
Cl3.2H2O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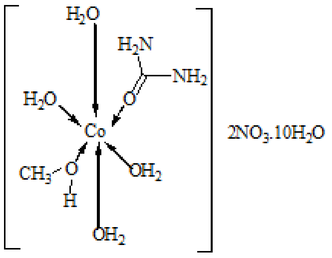
Wavenumber(cm⁻¹)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H2O
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Co
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O
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OH2
OH2
2NO3.10H2O

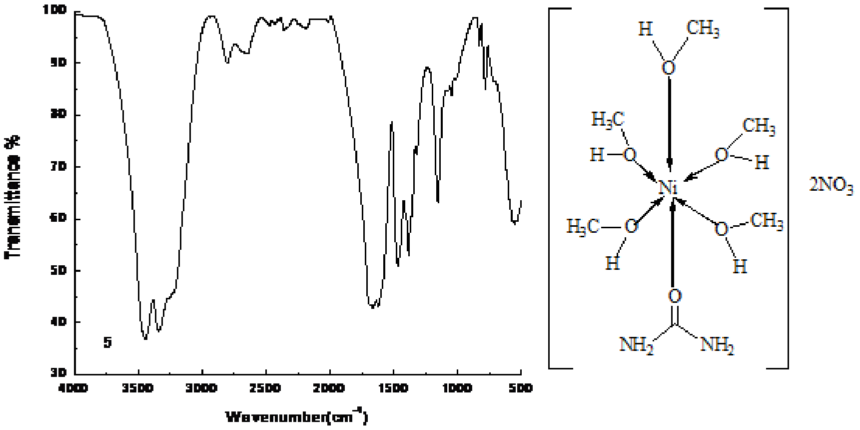

Fig. 2: Infrared spectra of urea complexes: $CrCl_3$.U. Me.$10H_2O$ (1), $MnCl_2$.U.Me (2), $FeCl_3$.U.Me.$6H_2O$ (3), $Co(NO_3)_2$.2U.Me.$14H_2O$ (4) and $Ni(NO_3)_2$.U.5Me (5)

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