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Structure and Properties of Some Metal-Urea Complexes Obtained at Low Temperature: Cr(III), Mn(II), Fe(III), Co(II) and Ni(II) Ions.

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ABSTRACT

The current work aims to synthesis and characterize the complexes of urea (U) with chromium(III), manganese(II), cobalt(II), iron(III) and nickel(II) ions at room temperature. The values of molar conductivity of the resulting complexes show that they are electrolytes in nature. The elemental, physical and spectral data were well explained in terms of the formation of $\text{CrCl}_3 \cdot \text{U} \cdot 8\text{H}_2\text{O}$ (1), $\text{MnCl}_2 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (2) $\text{FeCl}_3 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (3), $\text{Co}(\text{NO}_3)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (4), and $\text{Ni}(\text{NO}_3)_2 \cdot \text{U} \cdot 5\text{Me}$ (5) 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 complex formation of the metal ions toward urea was distinguished.

Keywords: Urea, Transition metals, Elemental analysis, Conductance.

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INTRODUCTION

Urea (Carbamide or carbonyldiamide) $\text{CH}_4\text{N}_2\text{O}$ is a white, odorless solid, highly soluble in water and ethanol, but insoluble in ether melts at 132°C , was first prepared by Wöhler [1] 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, as shown by the following reaction;



Urea may be prepared in the laboratory by the 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 $130\text{-}150^\circ\text{C}$. The carbamate is decomposed to form urea and water according to the following reaction;



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. 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]. 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. Complexes of urea with some metal ions are used as fertilizers [15-18]. Complexes of urea with zinc sulphate and nitrate, $[\text{Zn}(\text{CON}_2\text{H}_4)_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Zn}(\text{CON}_2\text{H}_4)_4](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ 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, $[\text{Ca}(\text{urea})_4](\text{NO}_3)_2$, [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]. Urea usually coordinates as a monodentate ligand through the oxygen atom, forming a $\text{C}=\text{O} \cdots \text{M}$ angle considerably smaller than 180° , in accordance with the sp^2 hybridization of the O atom. The rare N,O-bidentate coordination mode 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 atom [25]. Of particular chemical/biological interest is the ability of urea to undergo metal-promoted deprotonation [26]; the monoanionic ligand H_2NCONH^- adopts the μ_2 and μ_3 coordination modes. Urea and its derivatives such as the N,N'-dimethylurea and N,N'-diethylurea have only been found to coordinate as monodentate ligands through the oxygen atom. Raman and infrared spectra of urea have been observed by several investigators [27-37]. Urea possesses two types of potential donor atoms, the carbonyl oxygen and the two amide nitrogen. Penland et al. [38] studied the infrared spectra of urea complexes 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 [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, ($\nu(\text{C}=\text{O})$) 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]. In this paper, we report the synthesis, characterization, conductance and spectroscopic properties of urea complexes with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, MnCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ at room temperature.

EXPERIMENTAL

Reagents

Urea, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, MnCl_2 , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 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.

Synthesis of the metal-urea complexes

The complexes, $\text{CrCl}_3 \cdot \text{U} \cdot 8\text{H}_2\text{O}$ (**1**), $\text{MnCl}_2 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (**2**), $\text{FeCl}_3 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (**3**), $\text{Co}(\text{NO}_3)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (**4**), and $\text{Ni}(\text{NO}_3)_2 \cdot \text{U} \cdot 5\text{Me}$ (**5**) were prepared by mixing equal solutions of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (2.66 g, 0.01 mole), MnCl_2 (1.98 g, 0.01 mole), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.70 g, 0.01 mole), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g, 0.01 mole), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g, 0.01 mole) in 25 mL methanol with a 50 mL volume of urea solution (1.20 g, 0.02 mole) in methanol solvent. The mixtures were stirred for about 12 hours under refluxed system at room temperature *Ca.* 25°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.

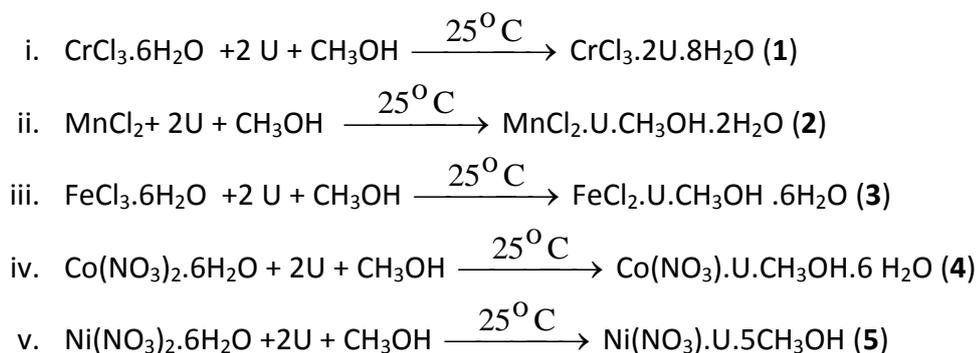
Measurements

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/5cm³ 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 ($4000\text{--}400\text{ cm}^{-1}$). The

electronic absorption spectra of urea complexes were recorded within 900–200 nm range using UV2 Unicam UV/Vis Spectrophotometer fitted with a quartz cell of 1.0 cm path length.

RESULTS AND DISCUSSION

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 complexes is in a good agreement with the general formulas CrCl₃.U.8H₂O (**1**), MnCl₂.U.Me.2H₂O (**2**) FeCl₃.U.Me.6H₂O (**3**), Co(NO₃)₂.U.Me.6H₂O (**4**), and Ni(NO₃)₂.U.5Me (**5**) complexes. The reactions can be represented by the stoichiometric equations:



The complexes are air-stable, hygroscopic, with low melting points, soluble in H₂O and dimethylsulfoxide, DMSO. The molar conductivities of (0.003 g 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 (91–213) Ω⁻¹ cm² 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 NO₃⁻ ions are precipitated with colored solution by adding of AgNO₃ or FeSO₄ 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 NO₃⁻ are present. These results establish the stoichiometries of these complexes, which are in agreement with the general formulas, were suggested.

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 prepared complexes at $T = 300$ K and their corresponding hybrid orbitals were calculated. The observed values of the effective magnetic moments μ_{eff} measured for these complexes agrees with the structures suggested, this is convenient with experimental values of 3.77B.M. [42], obtained for octahedral Cr(III) complex with d^2sp^3 hyperdization. The UV-visible spectra of the urea complexes given in Fig. 1 within the range 260-1000 nm and the band assignments were tabulated in Table 2.

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 [38]. 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 [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. 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 [38]. For all the prepared complexes, the coordination mode take place *via* oxygen of amide group (Fig. 3), 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 IR-active $\nu(M-O)$ vibration of all prepared urea complexes is observed at the range (540- 474) cm^{-1} [43, 44]. The band related to the stretching vibration $\nu(O-H)$ 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, $\delta(H_2O)$, 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 [45]. The stretching motion of ($\nu(N=O)$) is

observed at 1478 cm^{-1} and 1476 cm^{-1} as a strong band, while the bending motion of the type $\delta(\text{NO}_2)$ are well resolved and observed at 777 cm^{-1} and 785 cm^{-1} 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
$\text{CrCl}_3 \cdot \text{U} \cdot 8\text{H}_2\text{O}$ (1) 362.36 g/mol	Green	1:1	03.44 (03.31)	04.79 (05.52)	07.60 (07.73)
$\text{MnCl}_2 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (2) 325.91 g/mol	Light Pink	1:1	08.08 (07.36)	02.79 (03.68)	08.38 (08.59)
$\text{FeCl}_3 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (3) 362.3 g/mol	Yellow	1:1	06.20 (06.62)	05.09 (05.52)	07.13 (07.73)
$\text{Co}(\text{NO}_3)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (4) 383.03 g/mol	Pink	1:1	06.13 (06.27)	04.79 (05.22)	14.35 (14.62)
$\text{Ni}(\text{NO}_3)_2 \cdot \text{U} \cdot 5\text{Me}$ (5) 430.85 g/mol	Light Green	1:1	17.25 (17.89)	05.02 (05.96)	13.05 (13.90)

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

Complex	$\Lambda_m, (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$	μ_{eff}	Electronic spectra	
			Bands (nm)	Assignments
$\text{CrCl}_3 \cdot \text{U} \cdot 8\text{H}_2\text{O}$ (1)	213	3.77	266 438 624	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$ d—d, MLCT
$\text{MnCl}_2 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (2)	197	5.94	260 328 365	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$\text{FeCl}_3 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (3)	127	4.45	260 337	$\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$
$\text{Co}(\text{NO}_3)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (4)	200	4.37	311 534	$n \rightarrow \pi^*$ d—d, MLCT
$\text{Ni}(\text{NO}_3)_2 \cdot \text{U} \cdot 5\text{Me}$ (5)	91	3.32	308 410	$n \rightarrow \pi^*$ d—d, MLCT

Table 3: 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), $\text{CrCl}_3 \cdot \text{U} \cdot 8\text{H}_2\text{O}$ (1), $\text{MnCl}_2 \cdot \text{U} \cdot \text{Me} \cdot 2\text{H}_2\text{O}$ (2) and $\text{FeCl}_3 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (3) complexes.

U	A	B	1	2	3	Assignments ^(b)
3450	3390 3290	3440 3330	3440 3343	3478 3365	3467 3343	$\nu_{\text{as}}(\text{NH}_2)$ $\nu(\text{OH}); \text{H}_2\text{O}$
3350	3130 3030	3190	2051	3162	3125	$\nu_{\text{ss}}(\text{NH}_2)$
1683	1725	1505	1562	1587	1559	$\delta(\text{C}=\text{O})$
1471	1395	1505	1497	1477	1498	$\nu(\text{C}-\text{N})$

Table 4: 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), $\text{Co}(\text{NO}_3)_2 \cdot \text{U} \cdot \text{Me} \cdot 6\text{H}_2\text{O}$ (4) and $\text{Ni}(\text{NO}_3)_2 \cdot \text{U} \cdot 5\text{Me}$ (5) complexes

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

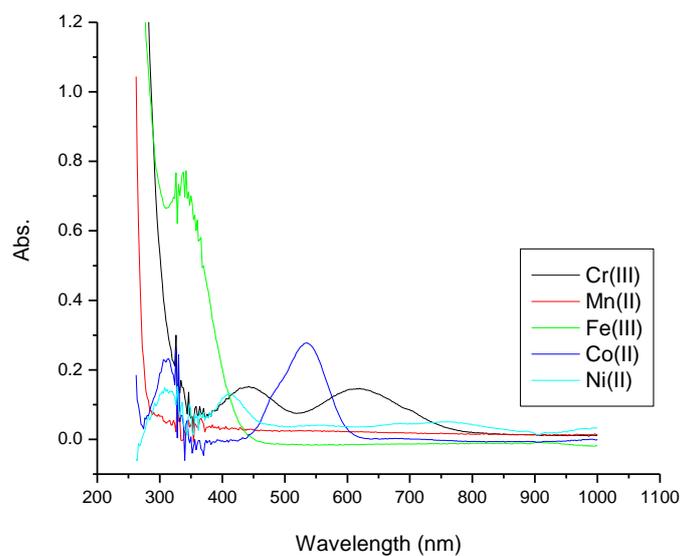


Fig. 1: UV-visible spectra of urea complexes.

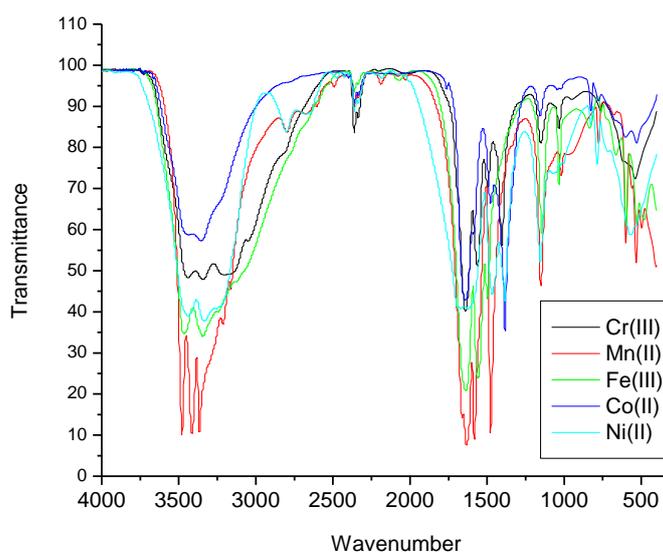


Fig. 2: Infrared spectra of urea complexes.

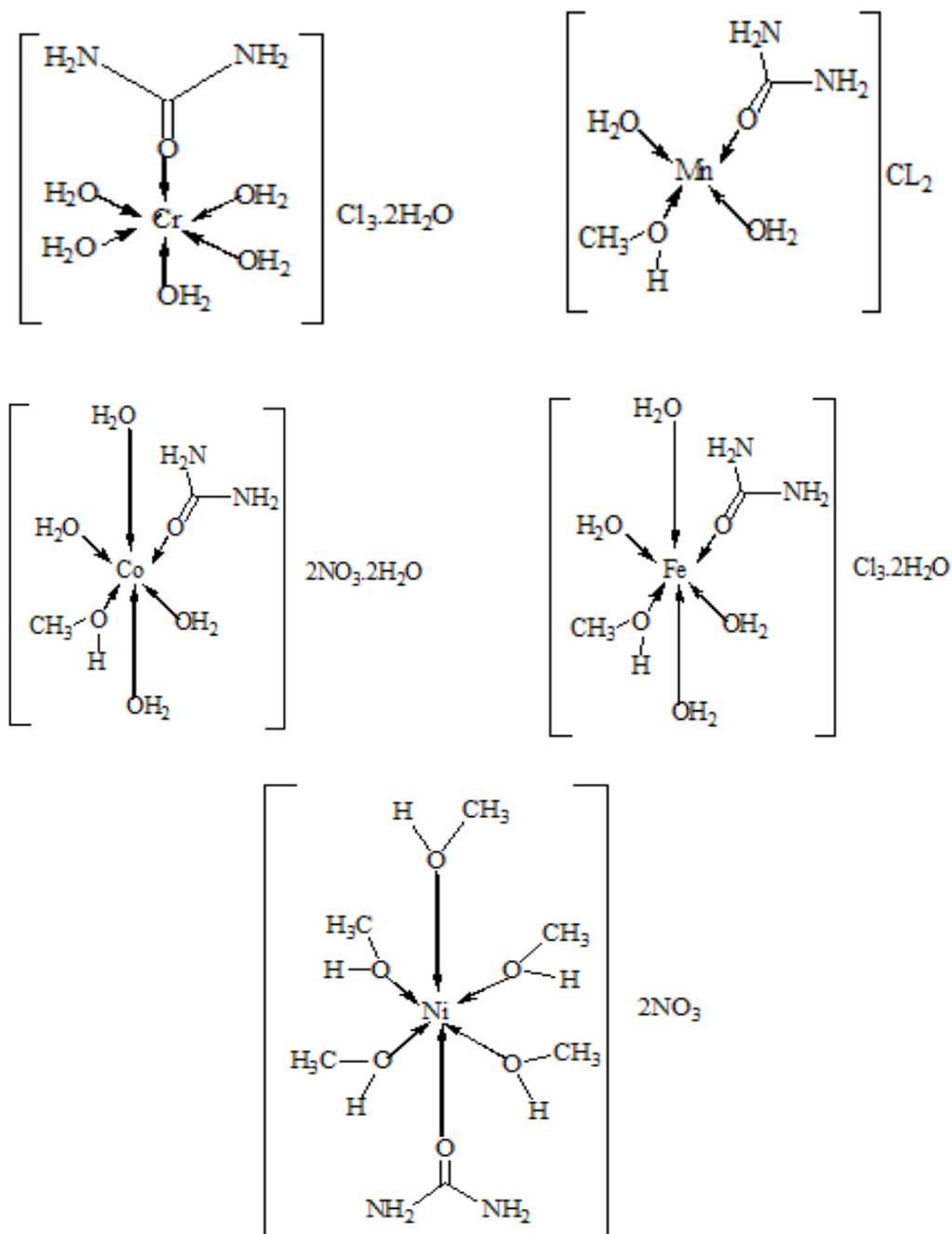


Fig. 3: Suggested structures of urea complexes.

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