Synthesis and thermal studies of Mn^{II}, Cr^{III} and Fe^{III} methionine complexes

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Abstract: The resulted complexes produced between Mn^{II}, Cr^{III} and Fe^{III} ions and biological molecules like amino acids play an important role in human life. Mn^{II}, Cr^{III} and Fe^{III} complexes are synthesized with methionine (MIE). These complexes were characterized by elemental analysis, molar conductance, infrared and UV-Vis spectra as well as thermogravimetric analysis (TGA/DTG). The elemental analysis introduce that the chelation ratio between metal ions and free methionine moiety behaves as bidentate ligand forming chelates with 1:2 (metal: ligand) stoichiometry for Mn^{II} ion and 1:3 for Cr^{III} and Fe^{III} ions. The molar conductance measurements of the products in DMSO indicate that the complexes are non-electrolyte nature. The activation energies and other kinetic parameters were calculated from the Coats-Redfern and Horowitz-Metzger equations.

1. Introduction

Amino acids are the principal building blocks of proteins and enzymes. They exist naturally in a zwitterionic state where the carboxylic acid moiety is ionized and the basic amino group is protonated [1]. Methionine with molecular formula, $C_5H_{11}NO_2S$, (Fig. 1) is one of the two sulfur containing amino acid, cysteine being the other [2]. Methionine helps to initiate translation of messenger RNA by being the first amino acid incorporated into the N-terminal position of all proteins. It is considered as an essential amino acid for normal Metabolism, growth and maintenance of body tissue. It is used as nutritional supplement and act as antioxidant in biological system [3-5]. Some metal complexes of DL–methionine were prepared in aqueous medium and characterized by different physico-chemical methods [6]. Methionine forms 1:2 complexes with metal, M(II). The general empirical formula of the complexes is proposed as $[(C_5H_{10}NO_2S)_2M^{II}]$; where M^{II} = Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). All the complexes are extremely stable in light and air and optically inactive. These transition metals are essential trace elements and used as nutritional supplement. They act as cofactors in various enzyme systems i.e. as metalloenzymes or as enzymatic activators [7-10]. Cd(II) and Hg(II) are toxic elements, that methionine is a biological chelating agent may lower the degree of toxicity for the formation of chelate with toxic metals [11]. The infrared and laser Raman spectra of L-methionine, L-methioninium perchlorate monohydrate were recorded at room temperature and the vibrational assignments of the observed wave numbers were made [12, 13]. A new palladium(II) complex with methionine was synthesized and characterized by a set of chemical and spectroscopic techniques [13] which indicate coordination of the amino acid to Pd(II) through the carboxylate and amino groups in a square planar geometry [14, 15]. In view of literature, the coordination chemistry of amino acids with different metal ions is a very interesting subject, so, in this paper, we report the formation of three methionine complexes in alcoholic solution. The aim of this study is to investigate the coordination behavior of methionine with Mn(II), Cr(III) and Fe(III) salts. Their synthesis, isolation and speculation by different spectroscopic studies are demonstrated.
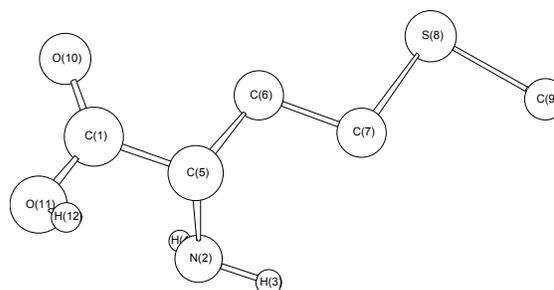
Fig. 1: Structure of methionine

2- Experimental
2-1- Material and instrumentation

All chemicals used were of the purest laboratory grade (Merck). Carbon and hydrogen percentages were determined using a Perkin–Elmer CHN 2400. Infrared spectra were recorded on Bruker FT-IR Spectrophotometer (4000–400 cm^{-1}) in KBr pellets. The UV–vis, spectra were studied in dimethylsulfoxide (DMSO) solvent with concentration (1.0×10^{-3} M) for the methionine and their complexes by help of Jenway 6405 Spectrophotometer with 1.0 cm quartz cell within the range of 800–200 nm. Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10 °C/min using a Schimadzu TGA– 50 H thermal analyzer. Molar conductance measurements of the methionine free ligand and their complexes with 1.0×10^{-3} mol/l in DMSO were carried out using Jenway 4010 conductivity meter.

2-2- Preparation of the complexes

The Mn(II) complex was synthesized by adding 2 mmol of $MnCl_2.H_2O$ in alcoholic solution to an 4 mmol alcoholic solution of methionine with molar ratio metal: ligand equal 1:2, at room temperature under stirring. The Mn(II) complex was precipitated as a brown powder, after constant stirring, at pH 8. The compound was filtered, washed with methanol and dried at 80 °C in an oven for about 2 hrs and the product was kept in a desiccate. The Cr(III) complex was synthesized by adding 2 mmol of $CrCl_3.6H_2O$ in alcoholic solution to an alcoholic solution of methionine containing 6 mmol of the ligand (molar ratio metal: ligand equal to (1:3), at room temperature and under stirring. The Cr(III) complex was precipitated as a green powder, after constant stirring, at pH 8-9. The compound was filtered, washed with methanol and dried at 80°C in an oven for about 2 hrs and the product was kept in a desiccate. The Fe(III) brown powder complex was synthesized by the same procedure of Cr(III) complex.

3- Results and Discussion

The complexes were characterized by different physicochemical techniques and some properties were investigated. The methionine Mn^{II}, Cr^{III} and Fe^{III} complexes were investigated in this study, are very stable at room temperature in the solid state. These complexes are insoluble in common organic solvents in cold or hot conditions except for DMSO solvent. No suitable crystals of the complexes were obtained in order to perform an X-ray structure determination. The elemental analyses and molar conductance of the free ligand and its complexes are given in Table 1. The analytical data are in a good agreement with the proposed stoichiometry of the complexes. The metal-to-ligand ratio in Mn^{II}, Cr^{III} and Fe^{III} complexes were different molar ratio, that found to be 1:2 or 1:3 (metal: ligand) in the coordination behaviors. All Mn^{II}, Cr^{III} and Fe^{III} complexes melted with decomposition far from the melting point of the free ligand (281 °C) owing to the formation of new compound with fitted with metal ions.

Conductivity measurements in non-aqueous solutions have frequently been used in structural studies of metal chelates 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, the higher will be its molar conductivity and vice versa. The non-ionized complexes have negligible value of molar conductance. The molar conductivities of the solid chelates are measured for 1.0×10^{-3} mol solution of 1:2 and 1:3 complexes in DMSO. The conductivity data reported for these complexes are given in Table 1. It is clear from the conductivity data that the complexes present behave as non-electrolytes [16] behavior. The molar conductivity values for all the complexes in organic solvent (DMSO) with 10^{-3} mol were in rang of (15-24) Ω^{-1} cm^{-1} mol^{-1} (Table 1).

Table 1: Elemental analysis and conductivity data for methionine complexes

Complexes	Mwt.	Λm ($\Omega^{-1}cm^{-1}mol^{-1}$)	Content (found) calculated		
			%C	%H	%N
$[Mn(C_5H_{10}No_2S)_2]$	351	15	34.18 (34.6)	5.74 (5.70)	7.97 (8.10)
$[Cr(C_5H_{10}No_2S)_3]$	496	25	36.28 (36.40)	6.09 (6.11)	8.46 (8.53)
$[Fe(C_5H_{10}No_2S)_3]$	500	22	36.00 (35.94)	6.04 (6.13)	8.40 (8.53)

The IR spectra in the (4000–400 cm^{-1}) region have provided information regarding the coordination mode in the methionine complexes (Fig. 2) and were analyzed by comparison with data for the free methionine ligand. The most relevant bands and proposed assignments for all the complexes are mentioned in Table 2. In the FT-IR spectra, extensive coupling occurs for several vibrations, making qualitative deductions about the environment around metal ions difficult. However, the IR spectral data (Table 2) shown changes in the position and profiles of some bands, as compared to those of free methionine, suggesting participation of the groups that produce these bounds in the coordination with Mn^{II}, Cr^{III} and Fe^{III} ions. Major changes are related to the carboxylate and amine bands. ligand methionine; amino acid physical properties indicate a "salt-like" behavior. In solution, the amino acid molecule appears to have a change which changes with pH. As intermolecular neutralization reaction leads to a salt-like ion called a Zwitterion. The amino group can lose a hydrogen ion to become negative charged, and also can accept a hydrogen ion to become positive charged. Assignment of observed frequencies; In all spectra, the characteristic band of NH_2 group vibration appears at 3300–3400 cm^{-1} corresponding to $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$. The band due to the NH_3^+ group $\nu(NH_3^+)$ at 3100, 2950 and 2500 cm^{-1} [17], which are very intense in the free ligand, appears as a weak shoulder or disappear in the spectra of the complex compounds. The tentative assignments have been done on the basis of standard references and some published papers [17, 18]. The characteristic bands of the complexes are listed in Table 2. The pattern of the IR spectra of other complexes is almost similar with each other with some exceptions. Most of the important bands in all the complexes were shifted significant compare to that of the free ligand which indicates the formation of new compound. The intensity of bands in the complexes has been reduced in most of the cases comparing the intensity of bands found in the free ligand. The reduction of absorption frequencies may be due to the formation of coordination bond through oxygen

atom of –COO group with metal ion. Since there is no significant absorption band at about 3450 cm^{-1} for v(O–H) absorption in any of the complexes, we can conclude that there is no water molecule in the complexes as coordinated water or as water of crystallization. In Cr(III) and Fe(III) complexes a weak significant absorption band is observed at about 3422, 3419 cm^{-1} which may be due to the O–H stretching vibration for the presence of moisture in the sample .

Table 2: The most significant FT-IR bands (cm^{-1}) of the methionine complexes

Complexes	v(N–H)(str.)	v(COO) (asym)	v(COO) (sym)	$\Delta(v_{as}-v_s)$
Mn(MIE)$_2$]	2917	1584	1408	176
[Cr(MIE)$_3$]	2947	1580	1413	167
[Fe(MIE)$_3$]	2947	1580	1413	167
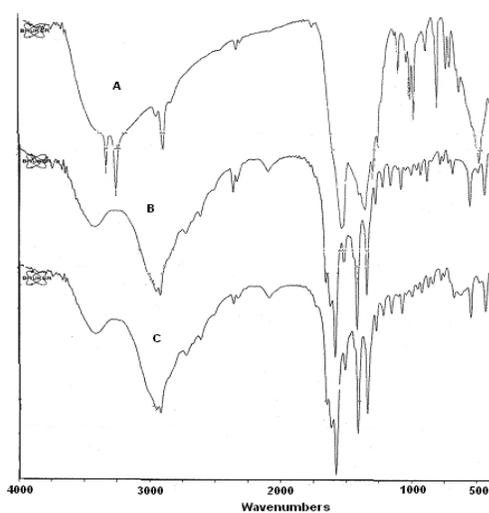
Fig. 2: IR spectra of (A): Mn(II), (B): Cr(III) and (C): Fe(III) methionine complexes

The characteristics absorption bands with tentative assignments of electronic absorption spectra of methionine complexes were demonstrated. The assignments have been done on the basis of some standard references [19-21]. The absorption bands located between 200 and 400 nm were assigned to the organic moiety and peaks above 400 nm was due to chelation. The bands due to π→π* transition in all metal complexes at 236–257 nm have broadening behavior, whereas in methionine it was found at about 236 nm. The presence of absorption band within 295–299 nm in methionine complexes was due to n→σ* transitions that was observed at 297 nm in ligand. The n→π* transition bands were observed at 318–365 nm (338 and 350 nm in free ligand) in almost all the metal complexes. The presence of π→π*, n→π* and n→σ* bands in all methionine complexes indicate the presence of the functional groups of the parent ligands (e.g. C=O, –NH$_2$ and C–S). A large shifting of the absorption bands in the complexes and appearing of a new band for d–d transitions also indicate the probability of forming M→L coordination bonds in the complexes. Transition metal complexes are generally colored and this color arises due to the absorption of light in visible region. Therefore, the band's centering around 413 nm in Mn(II), Cr(III) and Fe(III) complexes are clearly due to the d–d electronic transitions, which causes color of the complexes.

The structures of the methionine complexes (Fig. 3) accordingly the above interpretation using elemental analysis, molar conductance, (infrared and electronic) spectra as well as thermogravimetric analysis can be suggested as designed below.

Mn(II) methionine complex

Fe(III) methionine complex

Cr(III) methionine complex
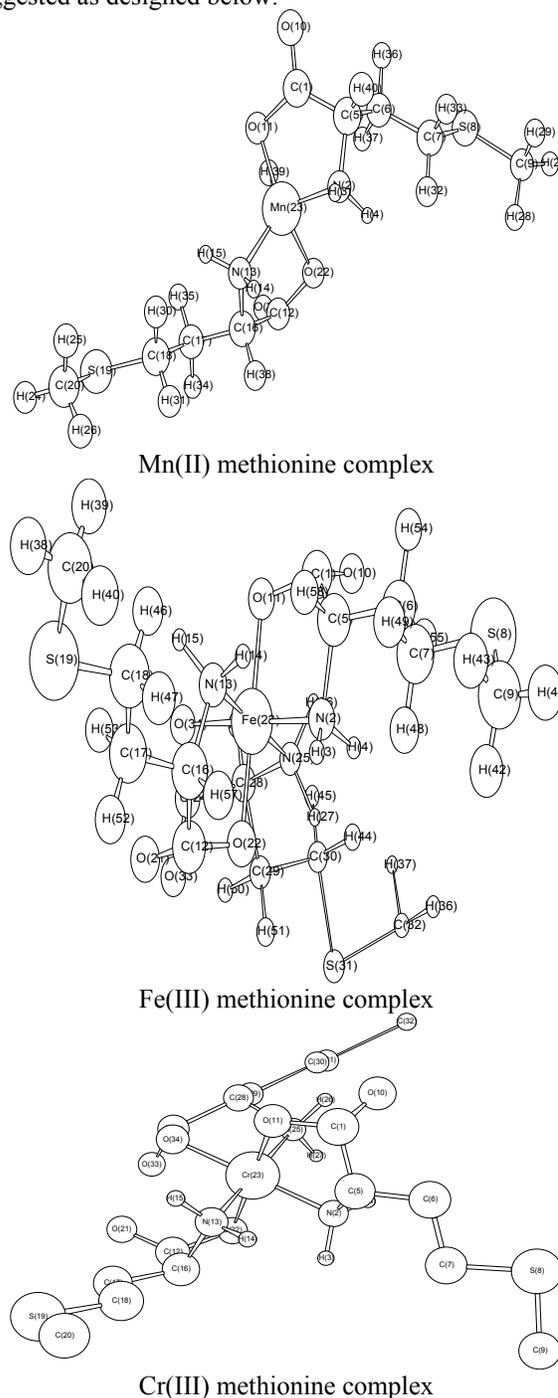
Fig. 3: Suggested structures of the methionine complexes
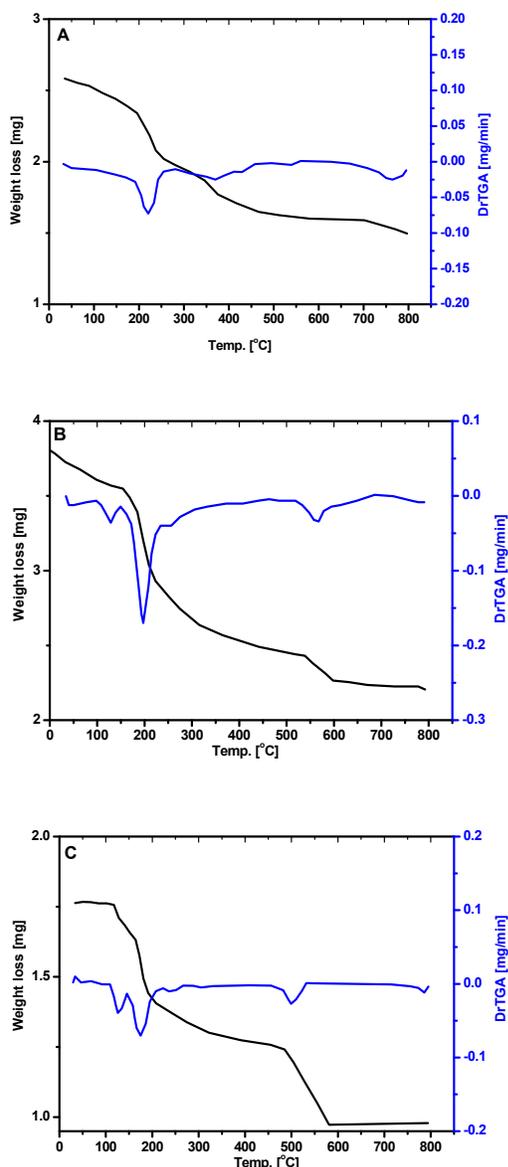
Fig. 4: TG/DTG curves of A- Mn(II)/methionine, B- Cr(III)/methionine and Fe(III)/methionine complexes.

The complexation between metal ions like (Mn(II), Cr(III) and Fe(III)) with methionine produced 1:2 and 1:3 molar ratio (metal: methionine) as a bidentate through its nitrogen of amino group and oxygen of carboxylate group which give general formula: $[M(MIE)_x]$, where MIE = methionine anion; x= 2 or 3. The TGA curves (Fig. 4) for methionine Mn(II), Cr(III), and Fe(III) complexes were carried out within a temperature ranged from room temperature until 800 ^{o}C. The calculated mass losses were estimated based on the TG data and agree quite well with the molecular formula of the suggested complexes. The decomposition stages, temperature ranges, maximum decomposition peaks DTG_{max}, percentage in mass loss, and the assignments of

decomposition moieties were discussed and assigned. The Mn(II) methionine complex gives four medium-to-weak stages of decomposition pattern. The temperature ranges within 50–230, 230–380, 380-440 and 750-800 °C with T_{max}= 230, 378, 436 and 770 °C, respectively. The total mass loss is about 40.75% due to loss of most organic moiety of methionine ligand, then leaving mixtures of manganese oxide (MnO_2) and few carbon atoms as a final residual. The thermal decomposition of chromium(III) complex is thermally decomposed in a successive four decomposition steps with definite maximum temperature at 125, 195, 560, and 780 ^{o}C. The found mass loss are 6.23%, 17.50%, 12.40%, and 6.90% at temperature range 50–125, 125–200, 200–560, and 560–800 ^{o}C, respectively. The final residual is become chromium(III) oxide polluted with unburned carbon atoms. Finally, the thermal decomposition of Fe(III) complex is thermally decomposed in a successive five decomposition steps. The total weight loss is to be 46.24% within the temperature range 50–800°C attributed to the loss most terminal groups of three molecules of chelating methionine. The final decomposition stage was leaving metal oxide contaminated with few carbon atoms which have a lack in oxygen atoms.

In recent years there has been increasing interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analysis of TG curves. Several equations [22-29] have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors [22-26] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [23], using

$d\alpha/dt = k(T)f(\alpha)$ (1)

Where α is the fraction decomposed at time t, k(T) is the temperature dependent function and f(α) is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function k(T) is of the Arrhenius type and can be considered as the rate constant k.

$k = A\ e^{-E^*/RT}$ (2)

Where, R is the gas constant in $(Jmol^{-1}K^{-1})$. Substituting equation (2) into equation (1), we get,

$d\alpha/dT =(A/\varphi\ e^{-E^*/RT})f(\alpha)$

Where, φ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form

$\ln g(\alpha) = - E^*/RT + \ln[AR/\varphi E^*]$

Where, g(α) is a function of α dependent on the mechanism of the reaction. The integral on the right hand side is known as temperature integral and has no closed for solution. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll [22] integral method of Coats-

Redfern [24], the approximation method of Horowitz-Metzger [27].

In the present investigation, the general thermal behaviors of the methionine complexes in terms of stability ranges, peak temperatures and values of kinetic parameters are tabulated Table 3. The kinetic parameters have been evaluated using the following methods and the results obtained by these methods are compared with one another. The following two methods are discussed in brief.

i- Coats- Redfern equation

The Coats-Redfern equation, which is a typical integral method, can be represented as:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dt$$

For convenience of integration the lower limit T_1 is usually taken as zero. This equation on integration gives;

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right]$$

A plot of left-hand side (LHS) against 1/T was drawn. E^* is the energy of activation in kJ mol^{-1} and calculated from the slop and A in (s^{-1}) from the intercept value. The entropy of activation ΔS^* in (JK^{-1}mol^{-1}) was calculated by using the equation:

$\Delta S^* = R \ln(Ah/k_B T_s)$ (3)
Where, k_B is the Boltzmann constant, h is the Plank's constant and T_s is the DTG peak temperature [29].

ii- Horowitz-Metzger equation

The Horowitz-Metzger equation is an illustrative of the approximation methods. These authors derived the relation:

$\log[\{1-(1-\alpha)^{1-n}\}/(1-n)] = E^*\theta/2.303RT_s^2$ for n≠1 (4)

When n = 1, the LHS of equation 4 would be log[-log (1-α)]. For a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

$\log[\log(w_\alpha / w_\gamma)] = E^*\theta/2.303RT_s^2 - \log 2.303$

Where, $\theta = T - T_s$, $w_\gamma = w_\alpha - w$, w_α = mass loss at the completion of the reaction; w = mass loss up to time t. The plot of $\log[\log(w_\alpha / w_\gamma)]$ vs θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor, A, was calculated from the equation:

$E^*/RT_s^2 = A/[\varphi \exp(-E^*/RT_s)]$

The entropy of activation, ΔS^*, was calculated from equation 3. The enthalpy activation, ΔH^*, and Gibbs free energy, ΔG^*, were calculated from; $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T\Delta S^*$, respectively.

Table 3: Kinetic parameters determined using the Coats–Redfern (CR) and Horowitz–Metzger (HM) of the methionine complexes.

Complex	Stage	Method	Parameter					r
			E (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
Mn(II)	1st	CR	1.01E+5	3.98E+8	-8.45E+1	9.71E+4	1.39E+5	0.9919
		HM	1.09E+5	4.45E+9	-6.44E+1	10.5E+4	1.37E+5	0.9888
Cr(III)	1st	CR	1.03E+5	3.21E+9	-6.67E+1	4.42E+4	1.31E+5	0.9980
		HM	1.13E+5	6.00E+10	-4.23E+1	10.9E+4	1.29E+5	0.9985
Fe(III)	2nd	CR	1.10E+5	5.41E+10	-4.28E+1	1.07E+5	1.26E+5	0.9764
		HM	1.15E+5	5.10E+11	-2.41E+1	1.11E+5	1.22E+5	0.9742

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