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THERMAL STUDIES OF MIXED LIGAND COMPLEXES OF ETHYL-α-ISONITRSOACETOACETATE AND DIENE

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Mixed ligand Ferrous (III), Chromium (III) complexes of Ethyl-α-isonitrosoacetoacetate and diene were prepared. Metal complexes were characterized by molar conductivity measurements, elemental analysis, FT-IR, UV-Visible spectroscopy, and thermal studies. The complexes are of 1 : 2 : 1 (metal : ligand : ligand) stoichiometry and are non-electrolytes in solution. The structural analysis indicates a six-coordinated M $(EINA)_2PPD$.

KEY WORDS : Ethyl-α-isonitrosoacetoacetate, Ferrous (III), Chromium (III), spectral studies.

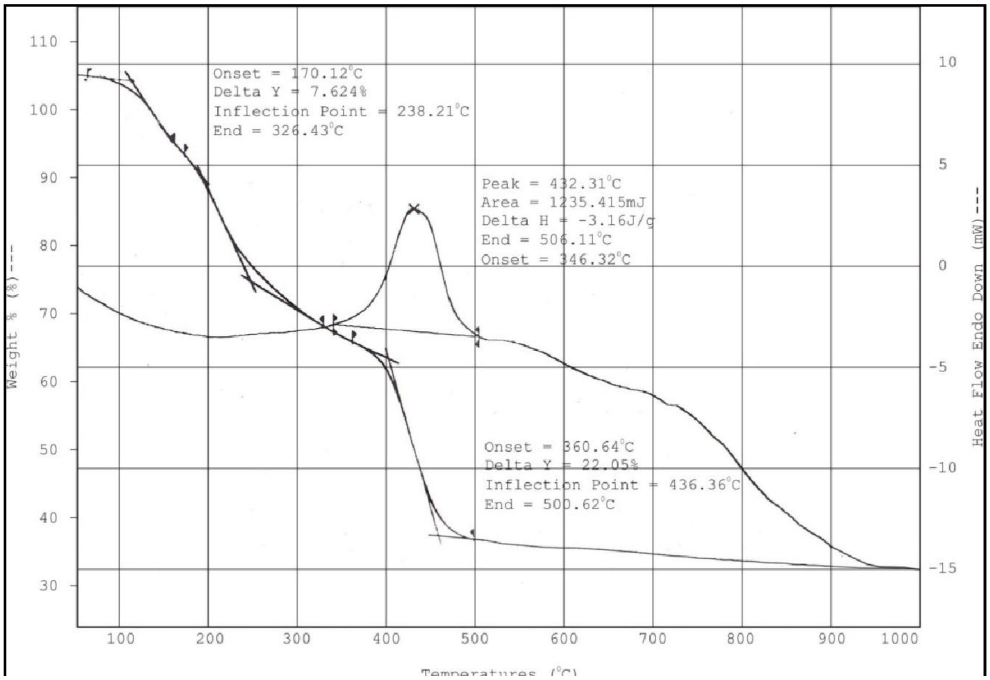
INTRODUCTION

Transition metal ions are playing an important role in biological processes in the human body [1, 2]. For example, nickel (II), copper (II) and zinc (II) ions are the most abundant transition metals in humans. They are found either at the active sites or as structural components of a good number of enzymes [3, 4]. The study of the coordination chemistry of biologically important metal ions with mixed ligands has been one of the recent developments in the field of bioinorganic chemistry. Metal complexes containing nitrogen and sulphur donors have been proved to be potential antibacterial and fungal agents [5] as well as component of several vitamins and drugs [6, 7].

We report here the synthesis, characterization and biological activities of some new Ferrous (III), Chromium (II) mixed-ligand complexes containing Ethyl-α-isonitrosoacetoacetate as ligands. The synthesized complexes are characterized by elemental, IR and electronic spectroscopic analysis.

EXPERIMENTAL SECTION

All chemicals used in this work were chemically pure, obtained from BDH chemicals. They include ferrous ammonium sulphate, Chromium acetate, sodium nitrite, ethyl acetoacetate para-phenyldiamine. The solvents used were ethanol, toluene deurated dimethyl sulfoxide (d6-DMSO), dimethyl formamide (DMF), chloroform.



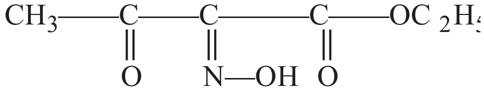
Thermogram of Cr(EINA)$_2$PPD

Synthesis of Ethyl-α-isonitrosoacetoacetate (HEINA)

Ethyl-α- isonitrosoacetoacetate (HEINA) is synthesized by the following procedure [8, 9].

Ethyl acetoacetate 1.4 moles and 3.5 mole of glacial acetic acid were taken in three naked round bottom flask fitted with thermometer, reflux condenser and mechanical stirrer and cooled in ice bath at 0° C and a solution of 95 % sodium nitrite was added over a period of one hour and temperature being kept between 5°C to 10°C. This mixture mixed with double distilled water, stirring for two hour and extracted with ether. After drying ether solution with sodium sulphate, the solvent was distilled off on a steam bath the crude product was dissolved in toluene and cooled to –13°C to –15°C. The separated white crystals were filtered, washed. The purity of the compounds was determined from the results of elemental analysis are summarized in Table 1. IR and ^{1}H NMR are analyzed.

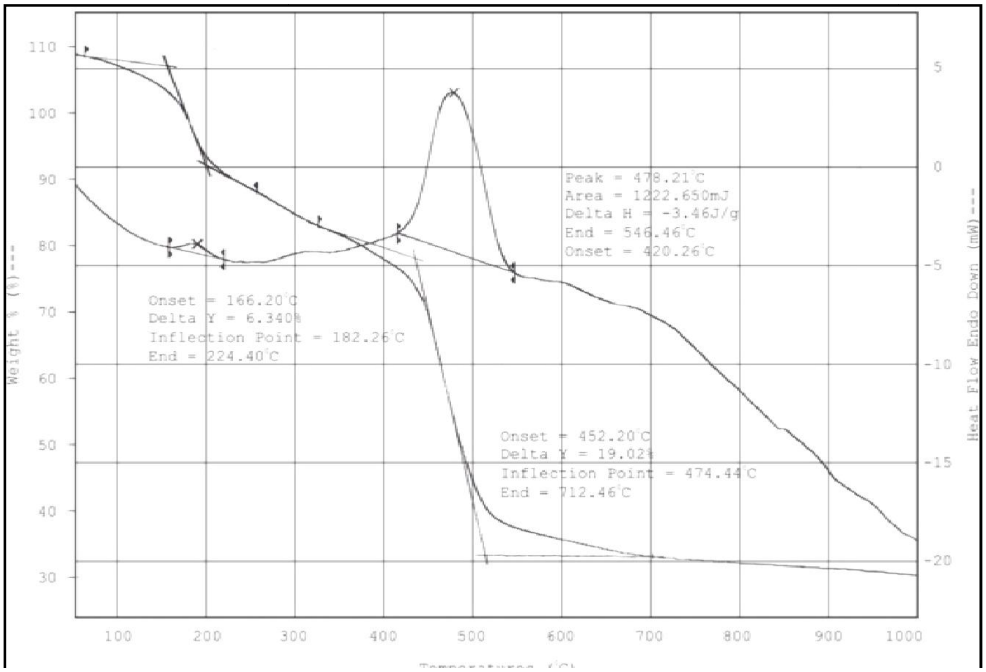
The resulting ligands have the following formula:



$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{N-OH}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OC_2H_5$$

Synthesis of the complexes

The 1 : 2 : 1 complexes were prepared by mixing a hot alcoholic solution of the HEINA (0.2 M) and para-phenyldiamine (0.1 M) with the calculated (0.1 M) of metal salt solution. The reaction mixture was refluxed for 4 hour. The pH of the solution was maintained at a value of 5.0-6.0 by the addition of dil NH$_4$OH/dil HCl. The solid complexes were dried on a steam bath with stirring, then filtered off and washed several times with alcohol. The solid complexes were dried and analyzed.



Thermogram of Fe(EINA)$_2$PPD

Physical Measurements

The FT-IR spectra recorded in the range 4000-400 cm^{-1} on a FT-IR spectrophotometer as KBR discs. The NMR spectra were measured using Varian Gemini 200-200 MHz spectrophotometer and the spectra were recorded from 0-15 ppm using TMS as an internal standard in dimethylsulfoxide (d6-DMSO) as the solvent. Thermal analysis (TG and DTG) were obtained in a nitrogen atmosphere using a type TGA 50 of Shimadzu deviatograph thermal analyzer. The molar conductivities were carried out using a Jenway 4310 conductivity meter. Electronic spectra were recorded in the range 200-800nm, on jasco V-530 UV-Vis, spectrophotometer.

RESULT AND DISCUSSION

Characterization of the Ligand

The structures of the complexes were established by the use of elemental analysis in Table 1, IR UV-Vis and ^{1}H NMR spectra. The infrared spectra of the ligand and the most important IR band assignments that affect the structural features are listed in Table 2. The different types of protons in EtOD of the complexes were obtained. The spectra of the ligand exhibit a sharp singlet signal at 8.651 ppm. The sharp singlet is observed at 2.330 ppm, 4.292 ppm and 1.296 ppm respectively. This signal is assigned to the aliphatic proton [10, 11] as shown in figure.

The electronic spectral band of the ligand scanned in different organic solvents is depicted in Ligand show three bands the first one at 206 nm referred to π-π^* transition. It splits into two strong bands 240 nm and 248 nm. This can be explained by presuming that the symmetric π electron system cloud of ligand becomes asymmetric by the dissociation of a proton.

Characterization of the Complexes

The solid complexes were subjected to elemental analysis and metal content, infrared (FTIR), ultraviolet and visible spectra (UV-Vis), magnetic susceptibility (μ_{eff}) and thermal analysis. The result of elemental analysis are given in Table 1 and are in good agreement with those calculated by the proposed formulae for 1 : 2 : 1 (M : L_1 : L_2) solid complexes.

Table 1. Elemental analysis and Magnetic moments for Fe^{3+}, Cr^{3+} complexes

Ligand complxes	**M : L**	**% calculated (Found)**				**ueff**
		C	**H**	**N**	**M**	
HEINA	--	45.30(45.28)	5.70(5.66)	8.78(8.80)	--	--
Fe(EINA)2PPD	1:2:1	45.18 (45.29)	6.27(6.32)	11.71(11.89)	10.87(11.12)	13.5
Cr(EINA)2PPD	1:2:1	44.72(44.80)	6.21(6.28)	11.59(11.99)	12.20(12.25)	12.8

Table 2. IR band assignment

Ligand complxes	**M : L**	**υ(OH)**	**υ (Ester C=O)**	**Y (Ketone C=O)**	**υ (C=N)**	**CH_3**	**$COOC_2H_5$**
HEINA	--	3441	1760	1745	1620	1418	1230
Fe(EINA)2PPD	1:2:1	3190	1700	1640	1602	1230	1109
Cr(EINA)2PPD	1:2:1	3457	1695	1660	1610	1420	1216

Table 3. Thermal Studies for Fe^{3+}, Cr^{3+} complexes

Complxes	**mol. wt.**	**Temp. °C**	**Weight loss**		**Probable Composition**
			Found	**calculated**	
Fe(EINA)$_2$PPD	477.99	200	6.33	6.42	Fe(EINA)$_2$PPD
		500	30.73	31.22	Fe_2O_3
Cr(EINA)2PPD	481.85	200	4.07	4.15	Cr(EINA)2PPD
		500	90.22	90.86	Cr_3O_3

Infrared spectral data of the complexes display interesting changes which may give a reasonable idea about these complexes. However, if these changes were interpreted in relation to elemental analysis, also the thermogravimetric analysis, molar conductance, electronic spectra and magnetic susceptibility measurements, the structure of the solid complexes may be clarified.

In the spectra of the complexes (Table 2) the band observed within the range 3190-3457cm^{-1} assigned to N–OH in the free ligand shifts to lower wave number in the complex indicating the coordination of N–OH to metal ion. The band observed within the range 1700-1695 cm^{-1} assigned to υC=O in the free ligand shifts to lower wave number (1690 cm^{-1}) indicating the involvement of the C=O group in chelation [12] Pathak and Haldar [13] have reported the Co–N vibration in tris (isonitrosoacetophenato) CO(III) at 620 cm^{-1}. Taylor and Talwar [14] have suggested that the band at 613 cm^{-1} in Pd(INA)2 may be attributed to the Pd-N vibration. It is therefore likely that the M-N vibrations in metal complexes of ligand would occur in the region 700-550 cm^{-1}.

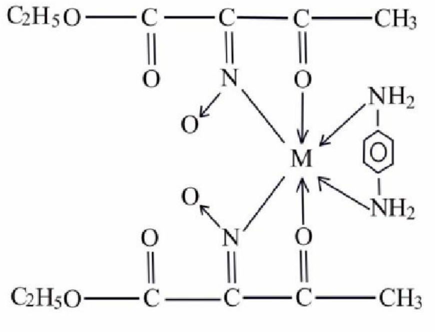
THERMAL ANALYSIS

TG analyses are very useful method for investigating the thermal decomposition of solid substances involving simple metal salts [15] as well as for complex compounds [16, 17]. The thermogram follows the decrease in sample weight with the linear increase in heat treatment temperature (10°C $\min^{-1}$) up to 800°C. The aim of the thermal analysis is to obtain information concerning the thermal stability of complexes as seen in Table 3. For $Fe(EINA)_2PPD$ complex a mass loss occurred within the temperature range 200°C corresponding to the loss of moisture. The TGA curve shows a drastic loss of weight in between 452 to 510°C which indicates the decomposition of the compound in this region (Inflection point 474.44°C). This interpretation is confirmed by the DTA curve which shows a strong exotherm at 478.21°C. At the end of the thermogram at higher temperature the metal oxide are formed as final product. The TGA curve of $Cr(EINA)_2PPD$ shows a initial weight loss in between 110°C to 200°C due to evaporation of moisture on heating the sharp decrease in weight at 426.36°C indicated decomposition of compound is further supported by DTA Curve which shows exothermic peak at 422.31°C. This significant loss in weight may be due to decomposition of compound which is also supported by DTA curve.

CONCLUSIONS

In the present paper, the data obtained from elemental analysis, FT-IR, electronic absorption spectra, Thermal analyses, molar conductivities and magnetic susceptibility measurements show that the complexes of Fe and Cr metal ions with ligand may be formulates are formed, where bonding in case of 1 : 2 : 1 complexes are formed through coordination with oxygen of the carboxyl group and nitroso group. The ligand HEINA acts as neutral bidentate ligand. The solid complexes prepared behave as non electrolytes in DMF solution. The electronic spectra of the ligands exhibits a CT band appears in the range 206-240-nm for the ligands. A shift to higher wavelength is observed on complex formation which may be attributed to M → L charge transfer spectra. The band observed in the spectra of the free ligands which may be ascribed to d-d electronic transition within the metal ions. The complexes exhibit an octahedral coordination with the ligand HEINA and para-phenyldiamine.

General structure for the metal ligand complexes is as shown below :



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