

Synthesis and characterization of newly Synthesized Transition Metal (II) Complexes with α -mercaptophenylacetohydroxamic acid

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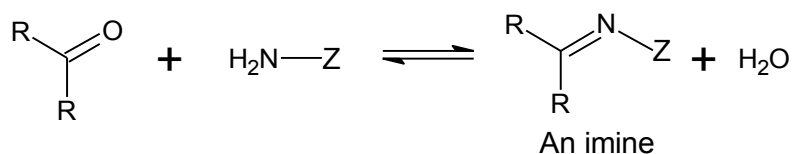
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ABSTRACT

In this paper we have reported the preparation of newly synthesized complexes of the α -mercaptophenylacetohydroxamic acid ligand with Fe (II), Co (II) and Ni (II) transition metal ions. The structures of the complexes have been confirmed by their elemental analysis and spectral analysis say IR, NMR and Electronic spectra of the complexes.

INTRODUCTION

Aldehydes and ketones react with primary amines and with other ammonia derivatives to form imines^{1,2}. An imine is a compound with a carbon-nitrogen double bond³.



As time passes Schiff bases have been selected as ligands for their complexation or chelation with metal ions to increase the positive biological properties or to decrease the negative biological properties by various researchers from national and international research institutes.

In this paper we have reported the preparation and elucidation of structures of newly synthesized complexes of the α -mercaptophenylacetohydroxamic acid ligand with Fe (II), Co (II) and Ni (II) transition metal ions.

EXPERIMENTAL

Preparation of Ligand α -Mercaptophenylacetohydroxamic Acid:

Preparation of methanolic KOH Solution-

A 56.1 g (1 mole) of KOH was dissolved in 140 ml of methanol with continuous stirring to prepared clear solution.

Preparation of Hydroxylaminehydrochloride Solution-

A methanolic solution of hydroxylaminehydrochloride was prepared by adding 46.7 g of it in 240 ml of methanol.

Preparation of Ligand-

Both freshly prepared solutions were mixed together keeping the temperature range at 40 °C. The mixture was left in ice-bath for five minute ensuring the complete precipitation of KCl. Thereafter 0.35 mole of 2-mercapto phenyl acetate was added in portions with constant shaking and after the addition; the solution was filtered immediately through solution. The

residue in funnel was washed with a little methanol. The filtrate was kept in Erlenmeyer flask for 48 hours. Crystals of potassium salt of the acid were filtered, washed with a little absolute alcohol and dried in air.

About half of the yield was mixed with 80 ml acetic acid of strength 1.25 N and stirred while heating until a clear solution was obtained. The solution was allowed to cool at room temperature and finally chilled in ice bath.

Thereafter, α -mercapto phenylacetohydroxamic acid was separated as light brown crystals.

Elemental analysis of the ligand is found as:

Ligand	% of C	% of H	% of N
Calculated	52.46	4.92	7.65
Found	52.08	4.89	7.48

Preparation of Complexes of α -Mercaptophenylacetohydroxamic Acid:

All chemicals such as transition metal (II) salts, ethanol, acetone, and methanol used in this study were of analytical grade. These chemicals were purchased from CDH or Merck and used as such.

Preparation of solution-

An aqueous solution of metal (II) salts of strength 0.01M were prepared by mixing appropriate amount of metal (II) salts in 40 ml of distilled water in a dried beaker with continuous stirring.

An ethanolic solution of ligand L^1H_2 was prepared by mixing 0.02 mole of ligand in 35 ml of ethanol in a dried beaker with continuous stirring.

Both solutions were filtered to remove any insoluble residue left.

Preparation of complex-

Ethanolic solutions of metal (II) salts solution were mixed with continuous stirring with a clear solution of the ligand in a dried beaker of 100 ml. After mixing, the reaction mixture was taken in a conical flask with constant shaking. The brown precipitate was filtered and washed successively with distilled water.

A solubility test of this complex was performed. It was found soluble in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF). It was sparingly soluble in water and insoluble in alcohol, ether and acetone. Its melting point was determined using open capillary tube in kjeldal flask filled with concentrated sulphuric acid. The elemental analysis of the complex is given as:

Elemental Analysis

Fe-complex	% of Fe	% of C	% of H	% of N
Calculated	12.25	42.12	4.39	6.14
Found	12.18	41.92	4.36	6.04

Co-complex	% of Co	% of C	% of H	% of N
Calculated	12.84	41.84	4.36	6.10
Found	12.52	41.48	4.32	6.01

Ni-complex	% of Ni	% of C	% of H	% of N
Calculated	13.89	42.42	3.78	6.62
Found	13.76	42.28	3.71	6.48

RESULTS AND DISCUSSION

The complexes of L^1H_2 with transition metal (II) ions say Fe (II), Co (II) and Ni (II) ions are anhydrous as supported by analytical and spectral studies. All these complexes are soluble in Water, alcohol and ether and insoluble in acetone, DMSO and DMF. The molar conductances of these complexes have been recorded in nitrobenzene in digital systonic conductivitymeter-304. All complexes are non-electrolytic in nature because they show very low value of its molar conductances. Magnetic moments of the complexes are in good agreement with the theoretical values calculated by Van-Vleck⁴. Analytical data, magnetic moment, molar conductance and color of all these complexes are given in following table.

S. No.	Complexes with Ligand	Colour	Melting point (in °C)	Λ_m ($Ohm^{-1}cm^2mol^{-1}$)	μ_{eff} (in B.M.)
1	[Fe(L^1H) ₂ (H ₂ O) ₂]	Brown	175	9.2	4.91
2.	[Co(L^1H) ₂ (H ₂ O) ₂]	Pink	190	9.2	3.89
3.	[Ni(L^1H) ₂]	Green	165	7.5	Dia.

Infrared and ¹HNMR Spectra:

IR spectra of the ligand and complexes were recorded in a Perkin-Elmer FTIR spectrophotometer using KBR pellet method. The IR spectral data of the ligand, their complexes and their assignments are given in following table.

Functional group	ν_{S-H}	ν_{C-S}	ν_{NH-OH}	ν_{M-S}	ν_{M-O}
Ligand	2600	710	3550
[Fe(L^1H) ₂ (H ₂ O) ₂]	670	3500	340	490
[Co(L^1H) ₂ (H ₂ O) ₂]	645	3445	330	470
[Ni(L^1H) ₂]	630	3420	310	440

The ligand has many donor sites such as carbonyl group nitrogen of amide and thiol. Generally, all amides exhibit two absorption bands⁵ at $\sim 1640\text{ cm}^{-1}$ related to $>C=O$ group, which is known as amide-I band and at $\sim 1600-1500\text{ cm}^{-1}$, which is known as amide-II. The amide-I band remain at same frequency in all complexes avoiding the participation of $>C=O$ group in coordination through the carbonyl oxygen of the ligand. The vibrational frequency of -SH group 2600 cm^{-1} in free ligand is absent in all metal complexes. It indicates the removal of proton before the participation of thiol group in complexation^{6,7}. The band at 3550 cm^{-1} responsible for NH-OH group in the spectra of free ligand is shifted to lower frequency $3420-3500\text{ cm}^{-1}$ in complexes. It indicates the lone pair of hydroxyl group involves in coordination⁸. The presence of two new bands at $310-340\text{ cm}^{-1}$ and $440-490\text{ cm}^{-1}$ in the spectra of metal complexes indicating the Metal-S and Metal-O bond in complexes^{9,10}. The broad absorption bands at 3450 and 3470 cm^{-1} in the spectra of Fe (II) and Co (II) metal complexes respectively provide the evidences in support of coordinated water molecules to central metal ion¹¹.

Electronic Spectra:

Electronic spectral data for the solution of transition metal (II) complexes are given in following Table.

Table:-Electronic spectral data along with band-assignment (in cm⁻¹) of “M(II)-L¹H₂” complexes

Complexes	Band Assignments	Bands (in cm ⁻¹)
[Fe(L ¹ H) ₂ (H ₂ O) ₂]	⁵ T _{2g} → ⁵ E _g	17685
[Co(L ¹ H) ₂ (H ₂ O) ₂]	⁴ F → ⁴ T _{1g} , → ⁴ T _{2g} and → ⁴ A _{2g}	18500, 21700 and 25300
[Ni(L ¹ H) ₂]	¹ A _{1g} → ¹ E _g , → ¹ A _{2g} → ¹ T _{2g} , and → ¹ T _{1g}	19270, 17385, 14640 and 13230

Transition metal (II) ions have no significant absorption in the Uv-Visible region. The absorption bands of transition metal (II) ions in the visible and near infrared region appears due to the transition from their ground states to the excited state of 3dⁿ-configurations¹². The Nephelauxetic ratio (β) has been determined by the method of Jorgenson¹³ using the relation:

$$(1 - \beta) = \frac{\nu_{aquo} - \nu_{complex}}{\nu_{aquo}} \dots \dots \dots (1)$$

The covalence factor (b^{1/2}), metal-ligand covalency percentage i.e. Sinhas parameter (δ%) and covalency angular overlap parameter (η) have been calculated by using following expressions¹⁴:

$$b^{1/2} = \frac{1}{2} [1 - \beta]^{1/2} \dots \dots \dots (2)$$

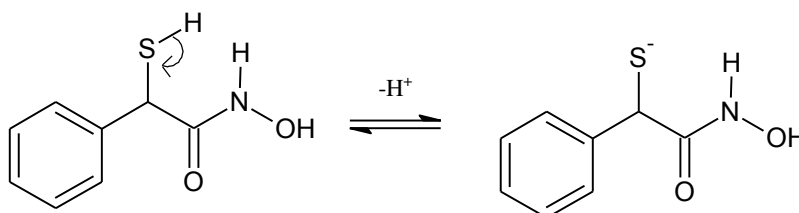
$$\delta\% = \left[\frac{1 - \beta}{\beta} \right] \times 100 \dots \dots \dots (3)$$

$$\eta = \left[\frac{1 - \beta^{1/2}}{\beta^{1/2}} \right] \dots \dots \dots (4)$$

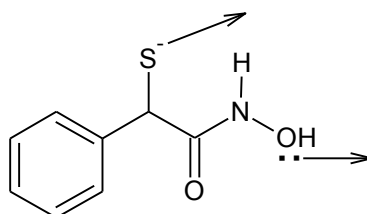
The +ve values of (1-β) and δ% supports the evidence of strong covalent bonding in all the synthesized chelated transition metal (II)-complexes¹⁵.

CONCLUSION

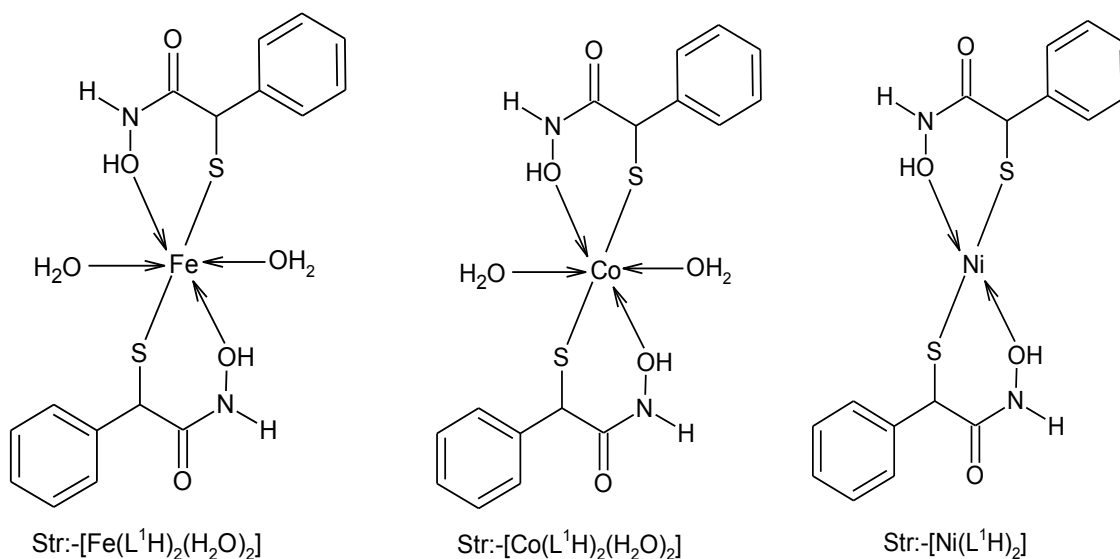
IR analyses of the ligands indicate ligand acts as uninegative bidentate ligand. Before ligation, ligands undergo deprotonation during condensation, which is interpreted as S-H singlet peak is absent in ¹HNMR spectrum of the ligands.



Coordination sites of the ligand may be shown as:



Elemental analysis shows that the complexes of Fe (II) ion and Co (II) ion with ligand have two ligands and two water molecules. Elemental analyses show that the complex of Ni (II) ion with ligand have two ligands only. Hence, structures of these complexes are as:



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