



Synthesis, compositional and spectral studies of some transition metal complexes with 3-aminolawsonoxime

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Abstract

The metal complexes which were synthesized from organic compounds containing oxygen and nitrogen donors are of great interest for structural study. The derivative of quinone, lawson (2-hydroxy-1,4-naphthoquinone) is natural coloring matter and is also indicated in the treatment of various ailment and diseases and as disinfectant. The hydroxyl derivative of 1,4-naphthoquinone is of great interest due to its slight therapeutic property. The general method is adopted for preparation of oxime, the ligand 3-Aminolawsonoxime (3-Amino-2-hydroxy, 4-keto 1-naphthoxime) was synthesized from 3-Amino-2-hydroxy-1, 4-Naphthoquinone. Some of the transition metal such as Fe, Co, Ni and Cu are in form of their salts were used for the complexation. The synthesized complexes were characterized by various physico-chemical techniques such as compositional studies and spectral studies. It has been found that the probable formulation of the complexes is $M L (H_2O)_2$. Wherein $M : L$ stoichiometry is 1:1. The spectral data while and magnetic studies of the metal complexes proposed distorted tetrahedral structure for Fe, Co and Ni complexes and square planer structure may be proposed for copper complex.

Keywords: Metal ligand complexes, Metal-oximes complexes, 1, 4-naphthoquinone derivative complexes.

Introduction

Now a days there has been growing interest in the structural study of the complexes derived from organic compounds containing oxygen and nitrogen donors with antimicrobial activity. Quinones are the naturally occurring materials in soil¹, plants² and animals³. It has important role in many biological electron transfer processes. In these processes they are reversibly reduced while divalent metal centers are oxidized. The derivative of quinone, lawsone (2-hydroxy-1,4-naphthoquinone) is coloring matter obtained from lawsonia alba (henna) indicated in treatment of various ailments and diseases and as disinfectant. Some of its derivatives show antimicrobial and antimalarial activities due to formation of metal complexes as intermediate.

The hydroquinone derivatives of 1,4-naphthoquinone class have been of great interest to us for sometime due to their mentioned as therapeutic agent in Indian drug system⁴⁻⁶. It has been established that the complexation characteristics of such quinone ligands can be changed at least in o-hydroxy p-naphthoquinone ligand by placing suitable substituent in quinonoid part^{7,8}. The systematic investigation on the metal complexes of o-hydroxy naphthoquinone derivative were studied in university of Pune. Some of the physical properties of 2-hydroxy-1,4-naphthoquinone monoximate of Ho(III) and Er (III) was reported by Jagtap et al⁹ while the coordination aspects of naphthoquinone derivatives towards various transition metal

have been extensively explored for better understanding of the structural peculiarities¹⁰⁻¹².

The complexes of transition metal and lanthanide with aminolawson (3-amino-2-hydroxy-1,4-naphtho quinone) were studied^{13,14}. The metal complex of bis-phthiocol monooximate Fe adducts was reported by Patil et al¹⁵. In present studies the transition metal complexes of 3-aminolawson oxime and its characterization is studied.

Materials and methods

Synthesis: All the ligands were prepared by using literature methods. Pierpont and Buchanan¹⁶ have provided a summarized account of preparative procedures for the metal complexes of quinone ligands. In the present study, our intention has been to characterize the resulting complexes formed using synthetic procedures which are essentially similar to the one described by Sawyer and Co-workers¹⁷. The starting material used was 2,3-dichloro-1,4-naphthoquinone (dichlone I) which was recrystallised from methanol. The hydrated metal sulphates and chlorides used were of high purity. The ligand was purified by recrystallization in the appropriate solvents and its purity was checked by M.P., TLC and elemental analysis.

Diclone: 2,3-Dichloro-1, 4-naphthoquinone (dichlone-I) (Cambrian Chemicals). It was recrystallized in methanol before use. Its purity was checked by melting point (Lit. m. p. 190⁰-192⁰C) and TLC.

3-Nitrolawsone (3N2HNQ): The nitro derivative 3-Nitro-2-hydroxy-1, 4-naphthoquinone (3-Nitrolawsone) was synthesized from dichlone (I). In this method 0.06 mole (13.32 gms) of dichlone and 0.2 mole (13.8 gms) of sodium nitrite were dissolved in a mixture of 75 ml methanol and 105 ml water in a round bottom flask. The solution was stirred to get precipitate of 2-hydroxy-3-nitro-1,4-naphthoquinone. The recrystallisation solvent of the compound was chloroform (Yield: 77.8%). C, H-Analysis for $C_{10}H_5O_5N$ gave observed values for percent carbon 54.56% and that of percent hydrogen is 2.69%. The theoretically calculated values are for percent carbon is 54.79% and that of percent hydrogen is 2.28%.

3-Aminolawsone (3A2HNQ): The amino derivative 3-Amino-2-hydroxy-1,4-naphthoquinone,(3-Aminolawsone) of 3-nitrolawsone was synthesized according to the method of Nagase, Matsumoto and others¹⁸ by reducing its nitro group to amino group.

In this method 0.0025 mole i.e. 0.55 gm. of 3-nitro-lawsone was suspended in 5.5 ml. water and while stirring 1.8 ml. of 10 percent sodium hydroxide was added to it. Sodium dithionite ($Na_2S_2O_4$) 1.6 gms was added during continuously stirring in the above reaction mixture. The temperature of reaction mixture was raised to about 50°C and was stirred for about half an hour. The reaction mixture was then filtered and the compound was washed with cold water when blackish powder of 3-Aminolawsone was obtained. After recrystallization from ethanol needle shaped blackish dark tan crystals were obtained (Yield: 42%). C,H-Analysis for $C_{10}H_7O_3N$ gave observed values for C = 63.41%, H = 3.80% and get matches with theoretically calculated values. The melting point is 234-236°C (decomp.)

3-Aminolawsoneoxime (3A2H5kO_x): The general method of preparation of oxime is adopted for the synthesis of ligand 3-Aminolawsoneoxime¹⁹. In which the carbonyl group at position 1 is replaced by oxime group. In this method 0.005 mole (0.945 gms) of 3-aminolawsone was dissolved in 10 ml of 2N solution of sodium hydroxide and was mixed with 0.75 mole (0.500 gms) of hydroxylamine hydrochloride in 10 ml. distilled water. The reaction mixture was maintained at 50-60°C for about half an hour with constant stirring¹⁹. The product of reaction was allowed to cool and neutralized by 2N solution of glacial acetic acid. After neutralization amino-lawsoneoxime was precipitated in the form of yellow crystals.

The obtained reaction mass was then filtered, washed with ice cold water and dried at room temperature under vacuum²⁰. The C, H- Analysis for $C_{10}H_8O_3N_2$ gave observed values the percent of carbon as 58.81%, while for percent of hydrogen 3.97%. These values get matches with theoretically calculated values .The decomposition temperature observed is 224°C.

Preparation of Metal Complexes: The transition metal complexes are synthesized by using common method¹⁹. In this ethanolic solution of ligand (3-Aminolawsoneoxime) 0.002

moles and aqueous solution of metal sulphate (0.001 mole in case of Ferrous sulphate hepta hydrate, Nickel sulphate hexa hydrate, while metal chloride (0.001 mole Cobalt chloride hexa hydrate and Copper chloride di hydrate) were de-aerated by passing dry and oxygen free nitrogen gas for about five minutes before mixing the solutions. The metal solutions were added slowly to ligand solution drop wise under nitrogen atmosphere in Schlenk: assembly with constant stirring. The reaction mixture was stirred for about two and half hours under the nitrogen atmosphere. The pH of the final reaction mixture was adjusted between 5 - 6.5 using 2N solutions of sodium hydroxide. Thereafter solid complex appears in the mixture. The reaction mixture was kept overnight in a refrigerator for maximum precipitation of the complex. The precipitated complexes were separated by filtration, washed with distilled water and then with ethanol and dried under vacuum at room temperature.

Physico-chemical measurements: Compositional Studies:

Analysis for C: The analysis for Carbon and Hydrogen was done in micro-analytical laboratory of Department of Chemistry, SP Pune University, Pune on Hosli C, H microanalysis instrument.

Spectral Studies: IR Spectra: The IR spectra of the ligand and metal complexes were recorded on Perkin Elmer Model 1600 FT-IR spectrophotometer at Department of Chemistry, SP Pune University, Pune.

Far IR Spectra: The Far IR spectra of the metal chelates were recorded on BRUKER IFS 66 V FT-IR spectrophotometer at RSIC, IIT, Chennai, using polyethelene support, in the region 600-50 cm^{-1} .

Electronic Spectra: The electronic spectra of metal complexes are recorded on UV-300 Spectrophotometer in the range 200-800 nm at SP Pune University, Pune

Result and discussion

Elemental Analysis: The synthesized metal complexes are observed in the form of the crystalline powder of brown black shade, non-hygroscopic. The complexes are insoluble in most of the common organic solvents such as ethanol, ether, toluene, benzene, acetonitrile, chloroform, carbon tetra chloride, dichloromethane, water etc. The insolubility of complexes in most of the organic solvents probably indicates that the complex may be polymeric in nature.

However these complexes are sparingly soluble in DMSO and DMF. The results of elemental analysis are presented in Table-1, which indicates that all the synthesized complexes are having M:L ratio 1:1 and contain two water molecules in their composition. Thus the probable formulation for complexes is M L (H_2O)₂. The conductivity measurements indicate the non-electrolytic behavior of all the complexes.

Table-1: Analytical data for some transition metal complexes of 3-aminolawsoneoxime (3-ALwOx)

Complex	Colour	Decomposition Temperature $^{\circ}\text{C}$	Elemental Analysis		
			C	H	M- Oxide
$[\text{Fe}(\text{NH}_2\text{LwOx})(\text{H}_2\text{O})_2]$	Dark black	379	39.98 (40.67)	3.41 (3.72)	28.6 (24.40)
$[\text{Co}(\text{NH}_2\text{LwOx})(\text{H}_2\text{O})_2]$	Dark black	354	38.76 (40.26)	3.76 (3.69)	23.08 (25.16)
$[\text{Ni}(\text{NH}_2\text{LwOx})(\text{H}_2\text{O})_2]$	Dark brown	403	39.79 (40.26)	3.63 (3.69)	28.95 (25.16)
$[\text{Cu}(\text{NH}_2\text{LwOx})(\text{H}_2\text{O})_2]$	Yellow brown	290	39.76 (39.66)	3.36 (3.63)	30.79 (26.28)

The brackets figures are theoretically calculated values. M- Fe/ Co/ Ni/ Cu.

Infrared Data: The infra red spectral data of ligand and corresponding metal complexes of Fe, Co, Ni and Cu is reported in Table-2. IR has played significant role in co-ordination chemistry of metal quinone compounds for the identification and assignment of the correct ligand oxidation state.

Assignment: It was found that substitution of any ionizable group in the quinonoidal part of the p-naphthoquinones gives rise to presence of bifurcated H-bond²¹ at least in solid state²². For example, lawsone, 2HNQ, exhibits two bands in its solid state null spectra where the broad absorption at lower wave number (3150 cm^{-1}) is due to intra- molecular H-bonding while the shoulder absorption at 3300 cm^{-1} corresponds in inter molecular H-bonded association²³. Similarly in 3A2HNQ one of the amino hydrogen forms a bifurcated H-bond, which is intra and inter molecularly bounded at the same time with carbonyl groups of the same ligand and a neighboring molecule respectively. The magnitude of either type of bonding in absence of any additional interactions is normally influenced by the inductive effects of C-3 substituents. Thus, the electron donor substituents are found to favor intra-molecular H-bonds while electron accepting groups induce more intermolecular association²⁴⁻²⁵. It is clear however; that as a result of the presence of bifurcated H-bonds in o-hydroxynaphthoquinones deciphering the effect of co-ordination on hydroxyl frequencies is a challenging proposition.

This is not the whole story, however coupled to the above mentioned difficulty is the possibility tautomerization of ortho-hydroxy 1,4-naphthoquinone into corresponding hydroxyl 1,2-naphthoquinones during complexation with metal, (a problem not encountered into solid state reactions but reality in solutions), and subsequent reductions of the quinone ligands²³.

The identification of the correct valence from the quinone ligand and its class, o-quinone or p-quinone, is an extremely difficult task in absence of the XRD-data but we have attempted it here on the basis of careful consideration of various properties and parameters of the synthesized complexes.

The infrared spectra of ligand and the metal (Fe, Cu, Ni and Cu) complexes are analyzed with specific reference to following frequencies which are directly concerned with effect of substitution and complex formation.

In the ligand, the strong broad band at 3300 cm^{-1} may be considered as combined effect of stretching vibration frequency of inter molecularly bonded oximino group and stretching frequencies of hydrogen bonded N-H. This band is observed in complex also.

The infrared spectra (Figures-1-5) of ligand and that of complexes with Fe(II), Co(II), Ni(II) and Cu(II) provide some information regarding mode of co-ordination in the complexes.

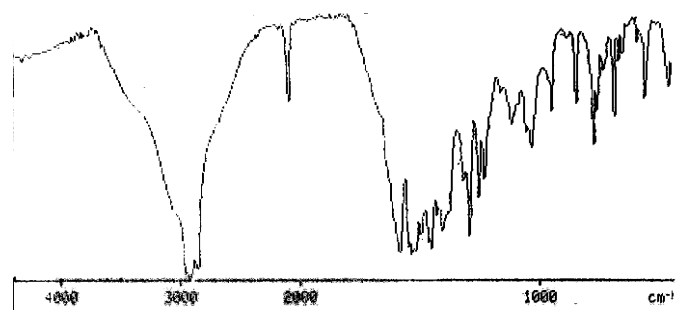


Figure-1: Infrared Spectra of 3ALwOx

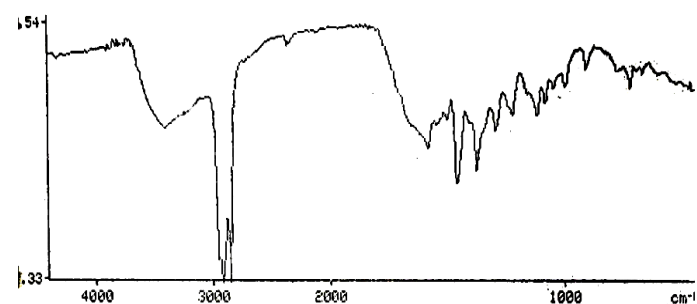


Figure-2: Infrared Spectra of Fe(II) Complex with 3ALwOx

The frequency observed at 3050 cm^{-1} in the ligand due to intermolecularly bonded phenolic group vanishes on complexation which is an indication of involvement of oxygen atom from the phenolic group in the co-ordination. The band at 1254 cm^{-1} ($\nu_{\text{C-O}}$ phenolic) in the ligand is affected on complexation due to the involvement of hydroxyl oxygen in bonding with metal. The frequency at 1537 cm^{-1} in ligand is attributed to $\nu_{\text{C=N}}$. Lowering of this frequency on complexation by about 33 cm^{-1} may be due to delocalization as expected in the reduced form of ligand. The strong absorption at 1057 cm^{-1} in the ligand is assigned to $\nu_{\text{N-O}}$. It is slightly increased by about 30 cm^{-1} on complexation which is common observation in metal oximates²⁶.

Since the synthesis has been carried out in presence of 2N NaOH there is a possibility of abstraction of proton from oximino OH group followed by the delocalization of the lone pair of electron at oximino oxygen atom which result in the reduction of quinone into semi-quinone. Abstraction of such oximino proton was already studied by Kumar²⁷. Due to facile electron transfer there may be a possibility of formation of 4-OH, 1,2 NSQ as reported by Rane et al.²⁸

This supports that oximino nitrogen acts as donor atom. The absorption at 1317 cm^{-1} which is attributed to $\nu_{\text{O-H}}$ phenolic in ligand, vanishes on complexation which is an indication of involvement of this oxygen in co-ordination. The absorption at 1230 cm^{-1} due to C – N and absorption at 3300 cm^{-1} due to N – H in the ligand remains as such on complexation.

The strong band at 1660 cm^{-1} observed in ligand due to free carbonyl group remains unaffected even on complex formation. The absorption bands between $1500\text{ cm}^{-1} - 1585\text{ cm}^{-1}$ are due to the normal aromatic vibrations. The frequencies between 1375 cm^{-1} to 1380 cm^{-1} in ligand as well as complex are attributed to activating effect of the carbonyl group on adjacent C=C vibrations. The most relevant bands and proposed assignments for the free ligand and complexes are listed in Table-2.

Finally from above spectral data we conclude that the co-ordination sites in the complexes are oximino nitrogen atom and 2-hydroxyl oxygen atom.

Far IR Spectra: We have extended the IR studies on present complexes to include region containing metal ligands vibrations in order to confirm the co-coordinating centers from the ligand and to examine the trends among the iso-structural complexes. The results of ligand and complexes with Fe (II) and Ni (II) are shown in Figures-6-8.

In the nitro series of complexes set of O_6 donating atoms is observed while in the amino series N_2O_4 and N_2O_2 sets are seen. The nitro series of complexes exhibits vibronically pure (or least coupled) $\nu_{\text{M-O}}$ frequencies at $580 - 680\text{ cm}^{-1}$ corresponding to $\nu_{\text{M-N}}$ linkages together with $\nu_{\text{M-O}}$ vibrations in the region $225 - 270\text{ cm}^{-1}$ are observed¹³.

The presence of $\nu_{\text{M-N}}$ band at 481 cm^{-1} has been reported by Nakamoto and Condrate²⁹ in case of copper amino acid complexes containing N_2O_4 chromophore such as ours. The $\nu_{\text{M-O}}$ mode is found to occur in the region $430 - 445\text{ cm}^{-1}$ and $220 - 245\text{ cm}^{-1}$. Also an additional absorption at $475 - 501\text{ cm}^{-1}$ corresponding to $\nu_{\text{M-N}}$ linkages is observed.

Electronic Spectra: Dimethylsulphoxide is use as solvent for recording these spectra. In transition metal quinone complexes electronic spectra are generally dominated by charge transfer (CT) transitions. The charge transfer transitions may be localized within the ligand molecule. The comparison of electronic spectral data of free ligand and that of corresponding metal complexes in dimethylsulphoxide indicate shifting of band position toward lower frequencies side as indicated in Table-3.

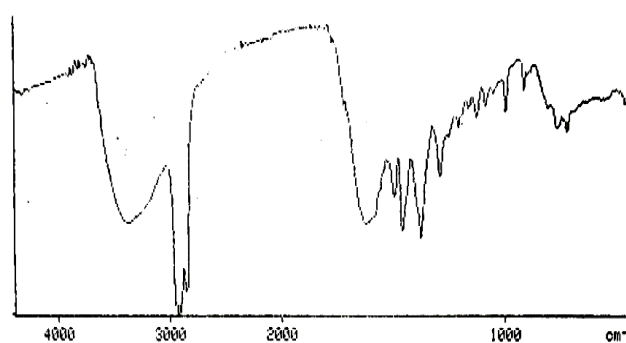


Figure-3: Infrared Spectra of Co(II) Complex with 3ALwOx

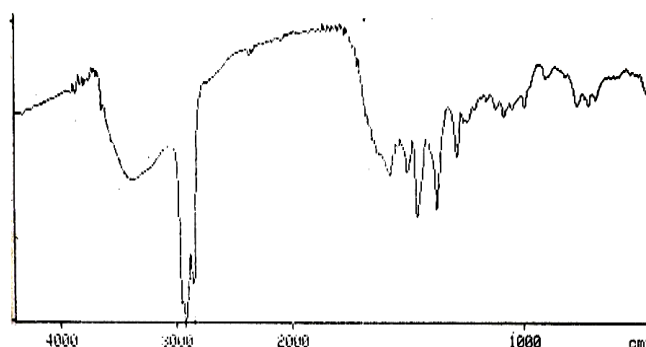


Figure-4: Infrared Spectra of Ni(II) Complex with 3ALwOx.

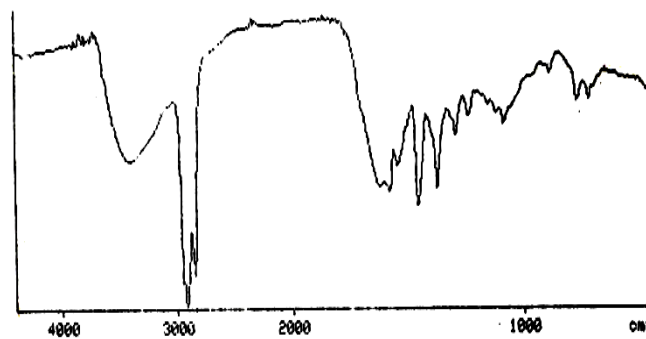


Figure-5: Infrared Spectra of Cu(II) Complex with 3ALwOx

Table-2: Significant peaks in the IR spectra of divalent Fe, Co, Ni and Cu complexes of 3-aminolawsoneoxime (3-ALwOx)

3-Amino-lawsoneoxime	Fe-Complex	Co-Complex	Ni-Complex	Cu-Complex	Assignment
3300(sh)broad Strong	3406	3384	3384	3406	ν_{O-H} inter of oximino gr. ν_{N-H} of NH_2 gr.
3050(sh)	-	-	-	-	ν_{O-H} intra of hydroxyl gr.
1666(sh)	1660(sh)	1708(sh)	1684, 1653	1718,1683 (sh.), 1641	$\nu_{C=O}$ gr.
1586(s)	1585	-	1577	1582	$\nu_{C=O}$ (quinone)
1537(m) 1519	1535 1504	1535 1498	1535 1506	1544 1505	$\nu_{C=N}$ (oximino)
1317	-	-	-	-	ν_{O-H} (phenolic)
1254	1240(sh)	1250(sh)	1243	1239(b)	ν_{C-O}
1230	1221	1208	1217(w)	1207(m)	ν_{C-N}
1057 1034	1081 1046	1086	1086	1086	ν_{N-O}
- -	534(w) 228	541.530 208(w)	543 206	540(w) 220	ν_{M-O}
-	490(b)	501	479(b)	483(b)	ν_{M-N}

Table-3: Electronic spectral frequencies for ligand and metal complexes

Ligand (L)	Frequencies in cm^{-1}				Probable Assignment
	Fe(II)- L Complex	Co(II)- L Complex	Ni(II)- L Complex	Cu(II)-L Complex	
37735	38461	38461	38461	38461	$\Pi \rightarrow \Pi^*$
35714	36363	36363	36363	36383	$\Pi \rightarrow \Pi^*$
21739	25000	25000	25000	24390	Charge Transfer

L= 3-Aminolawsoneoxime

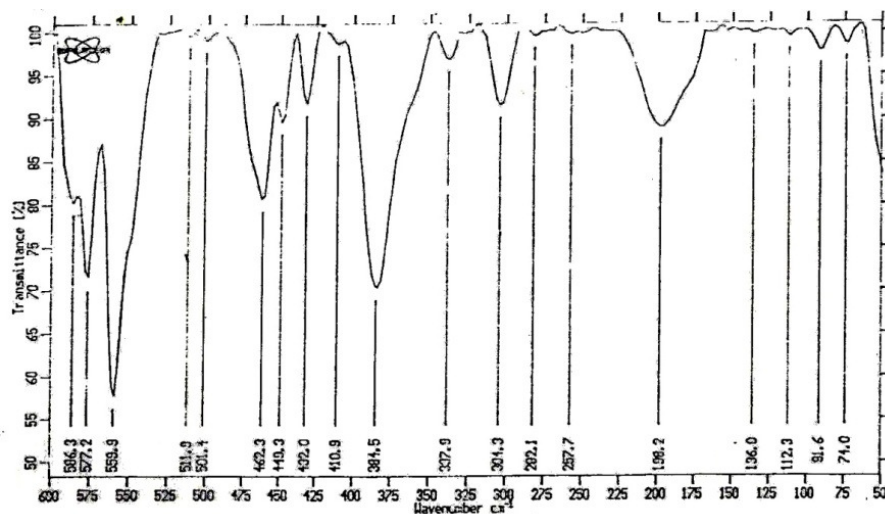


Figure-6: Far Infrared Spectra of 3ALwOx

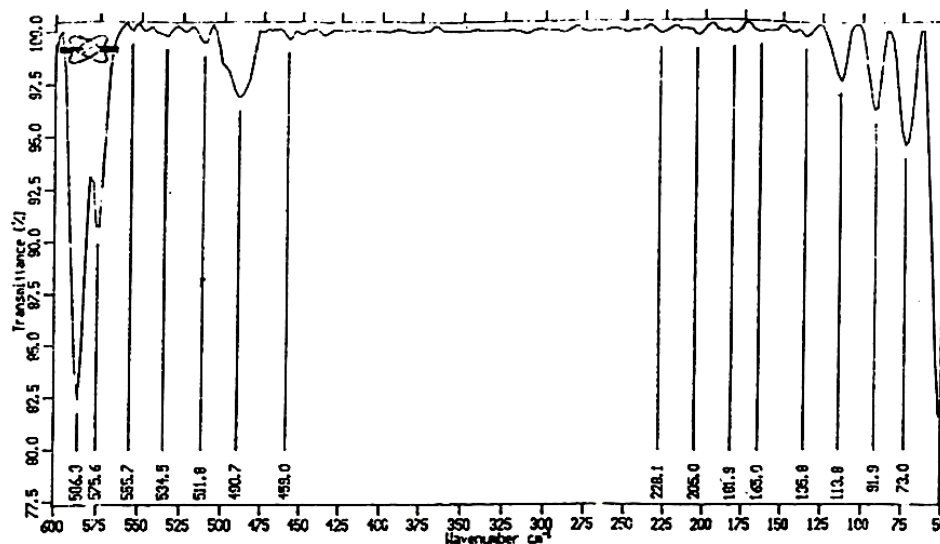


Figure-7: Far Infrared Spectra of Fe(II) Complex with 3ALwOx

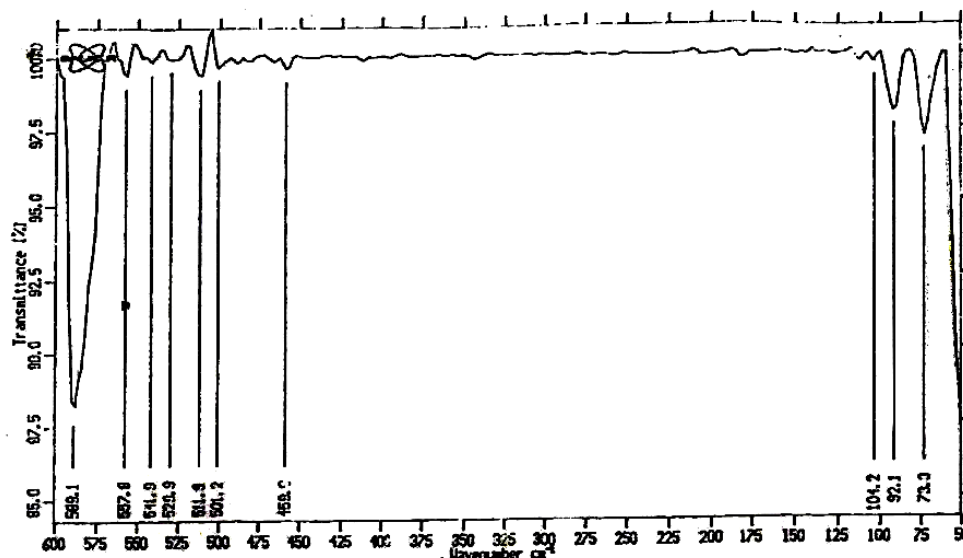


Figure-8: Far Infrared Spectra of Co(II) Complex with 3ALwOx

The absorption frequencies in ligand are observed at 265 (37735 cm^{-1}), 280 (35714 cm^{-1}) and 460 nm (21739 cm^{-1}) on the other in metal complexes the absorption appears at 260, 275 and 400 nm. The bands around 265 and 280 nm are assigned to ligand based localized n to π^* transition while the band around 400 nm may be due to charge transfer³⁰. The charge transfer band shifting toward lower wave number side may be due to co-ordination of the 3ALwOx to the metal atom.

Conclusion

The synthesized ligand 3-aminolawsoneoxime was used in complexes formation. The four metal complexes of divalent metals viz. Fe, Co, Ni and Cu were synthesized using ligand. These complexes were characterized by physicochemical

techniques. On the basis of elemental analysis for the complexes tentative composition of complexes is shown to be $ML(H_2O)_2$ wherein $M : L$, stoichiometry is 1 : 1 and tetra coordination is proposed. The infrared and far infrared spectral studies are used for fixing the co-ordinating sites of the ligand. The shifting of ν_{N-O} band to higher value on complexation is an indication of the oximinonitrogen acting as donor atom. While the disappearance of the ν_{O-H} phenolic band in ligand on complexation shows the ionization of phenolic O-H and the involvement of this oxygen in co-ordination with metal. The electronic spectral data for the complexes coupled with magnetic studies suggest that square planer structure may be for copper complex while distorted tetrahedral structure for Fe, Co and Ni complexes.

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