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# Interaction of Salicylamide and Salicylic Acid with Iron and Cobalt and their Comparative Study by IR and NMR

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**Abstract:** *The complexes formed by salicylic acid and several substituted derivatives of salicylic acid (Salicylamide) with essential metal ions of the soil (iron and cobalt) have been investigated at 25° and in a medium of variable ionic strength using pH. The equilibrium constants of complex formation of the 1 : 1 , 1 : 2 and1 : 3 mole ratio metal–acid complexes formed are discussed with reference to the activity degradation of substituents. Salicylic acid and Salicylamide after disposal can also react with the various metal ions present in the soil to form complexes. The rate at which these complexes are formed is done with the help of UV-vis. Spectroscopy. The complexes formed are characterized by various Spectroscopic technique viz. FTIR and NMR.*

**Keywords:** Salicylic acid, Salicylamide, FTIR, UV-vis.

## I. INTRODUCTION

Salicylic acid is a stable chemical compound, but just as the name "acid" does not implies that it is a dangerous chemical. It is used treat the skin diseases of the skin. It is generally used in specific laboratory and medical assays. Contrast change in the physical nature of two compounds has drawn the attention towards comparative study of them. Salicylic acid, a naturally occurring plant hormone, is an important signal molecule known to have diverse effects on biotic and abiotic stress tolerance [1] . Salicylic acid is used in treating the acne because of its ability to penetrate the follicle. Salicylic acid and its derivatives have the ability to form chelating compounds with metal ions. They have outstanding biological significance in which anti-rheumatic and anti-fungal actions are the one, instead of this they have toxic action to man in higher dosage. [2] The natural sources of salicylic acid are unripe fruits and vegetables, particularly blackberries, mushrooms and chicory. Salicylamide is the common name for the substance o-hydroxybenzamide (OHB), or amide of salicyl. Salicylamideis a non-prescription drug with analgesic and antipyretic properties. Its medicinal uses are similar to those of aspirin [3] Salicylamide is an important fine chemical intermediate, acts as a non-steroidal anti-inflammatory agent with analgesic and antipyretic properties, which is an effective drug for analgesic use as well as in combined medicines for symptoms associated with cold and influenza [4, 5] . Salicylic acid and its derivatives are associates with diverse pharmaceutical activities such as antibacterial, insecticidal, fungicidal, antimicrobial, antagonist, anthelmintic, anti-inflamonatary, etc. Beside the activities, active ingredient and their metal complexes are also used as/in medicine. Salicylamideis also one of the derivatives of salicylic acid; it also has got many properties similar to salicylic acid. Presently, the preparation of derivatives of Salicylamide and Salicylic acid is done using metals such as iron (Fe) and cobalt (Co) to prepare the metal chelates of the complexes. Salicylamide is an important fine chemical intermediate, which has versatile applications in the production of dyes, pigments, pharmaceuticals and spicery. Salicylamide acts as a non-steroidal anti-inflammatory agent with anal esic and antipyretic properties, which is an effective drug for analgesic use as well as in combined medicines for symptoms associated with cold and influenza [6, 7] .

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## III. SCOPE AND PURPOSE

Salicylic acid is a stable chemical compound, but just as the name "acid" does not implies that it is a dangerous chemical. It is used treat the skin diseases of the skin. It is generally used in specific laboratory and medical assays. Contrast change in the physical nature of two compounds has drawn the attention towards comparative study of them. Salicylamideis used by various chemical and pharmaceutical industries as making drugs for reducing sugar and for making pesticides. It is used for making insecticides and also pesticides it act as pollutant. In this regard complexation of the compound may play an important role. The active sites of SA and SAM (i.e. carboxylic part and phenolic part and amide part in case of SAM.) are also good ligating sites. It is therefore interesting to optimize condition for the complexation reaction and its reactivity towards metal ion in terms of rate of reaction while forming the metal complexes, which will further help us to understand the complexation tendency of the ligand. The study may play important role for both the detection and decomposition purposes. Salicylic acid and Salicylamide after disposal can also react with the various metal ions present in the soil to form complexes. The rate at which these complexes are formed is done with the help of UV-vis. Spectroscopy. The complexes formed are characterized by various Spectroscopic technique viz. FTIR and NMR.

## IV. CHEMISTRY

### 4.1 Purification of Ligands, SA and SAM

SA and SAM was purified by using different laboratory techniques viz. solid-liquid extraction with acetone, then with column chromatography on alumina eluted with benzene-chloroform mixture (1:1) followed by crystallization in chloroform-diethyl ether mixture as shown below in figure 1.

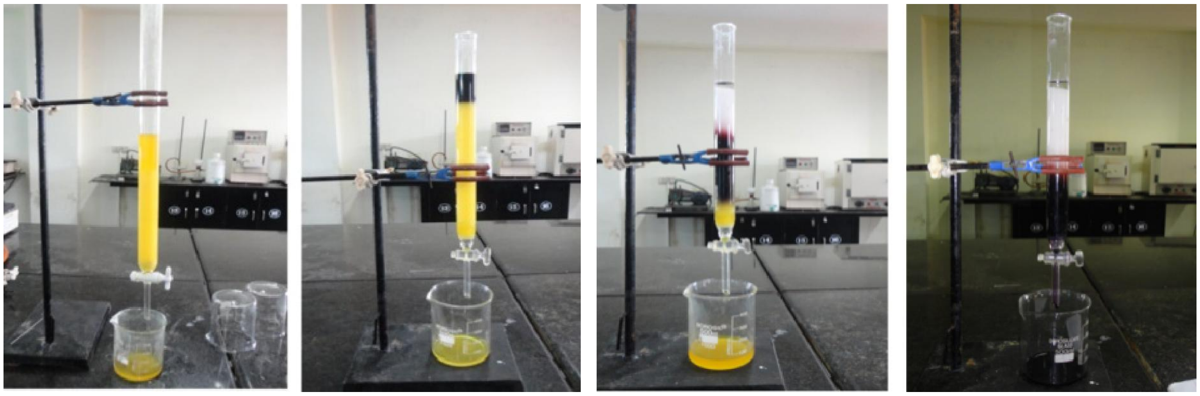

**Figure 1:** Column chromatography

### 4.2 Synthesis of Metal Complexes of SA and SAM with Fe (III) Chloride

Synthesize Iron complex of SA and SAM by reacting 1:3 molar ratio of Ferric chloride and of SA and SAM respectively. 0.41gms.(0.1mmol) of SA/ SAM is taken and then dissolved in 10ml of methanol in 3 necked round bottom flask having capacity 100 ml. It was simultaneously heated and magnetically stirred continuously over a hot plate equipped magnetic stirrer. After complete dissolution of the solution, 0.16 g of Ferric chloride in 10ml of methanol is added. The mixture was left it to stirring for 7-8 hours at about 40-43 0 C in a solvent methanol. NaOH is added drop wise in a solution. After the reaction is completed, the reaction mixture is allowed to crystallize by keeping the reaction mixture over night till whole the solvent is evaporated. The crystals obtained are recrystallized so that the impurity presents (ligand or metal) are removed and the pure crystals are obtained. The crystals obtained are dried in the own at minimum temperature (&lt;40 º C).

### 4.3 Synthesis of Metal Complex of SA and SAM with Co (II) Chloride

Synthesize Cobalt complex of SA and SAM by reacting 1:3 molar ratio of Cobalt chloride and of SA and SAM respectively. 0.41gms.(0.1mmol) of SA/ SAM is taken and then dissolved in 10ml of methanol in 3 necked round bottom flask having capacity 100 ml. It was simultaneously heated and magnetically stirred continuously over a hot plate equipped magnetic stirrer. After complete dissolution of the solution, 0.23 g of Cobalt chloride in 10ml of methanol is added. The mixture was left it to stirring for 7-8 hours at about 40-43 0 C in a solvent methanol. NaOH is added drop wise in a solution. After the reaction is completed, the reaction mixture is allowed to crystallize by keeping the reaction mixture over night till whole the solvent is evaporated. The crystals obtained are recrystallized so that the impurity presents (ligand or metal) are removed and the pure crystals are obtained. The crystals obtained are dried in the own at minimum temperature (< 40 º C).

## V. RESULTS

### 5.1 Solubility

The comparison of solubility of Salicylic acid and Salicylamide in different solvents is studied and is observed that these ligands are soluble in polar solvent and insoluble in nonpolar solvents and most of solvents are that in which both show same solubility.

| S. No. | Solvent | Salicylamide | Salicylic acid |
|---|---|---|---|
| 1. | Diethyl ether | Not Soluble | Not Soluble |
| 2. | Dichloro Methane | Not Soluble | Not Soluble |
| 3. | Acetone | Soluble | Soluble |
| 4. | Chloroform | Not Soluble | Not Soluble |
| 5. | Methanol | Soluble | Soluble |
| 6. | Hexane | Not Soluble | Soluble |
| 7. | Ethyl Acetate | Soluble | Soluble |
| 8. | Ethanol | Soluble | Soluble |
| 9. | Benzene | Not Soluble | Soluble |
| 10. | Acetonitrile | Not Soluble | Soluble |
| 11. | Water | Partially Soluble | Partially Soluble |
| 12. | Acetic acid | Soluble | Soluble |
| 13. | Dimethylsulphoxide | Soluble | Soluble |

**Table 1:** Comparative solubility of SA and SAM in different solvents

### 5.1.1 Solubility test of Metal Complexes of Salicylamide

The solubility of the metal complexes of Salicylamide is tabulated in table 2.

| S. No. | SOLVENT | Fe | Co |
|---|---|---|---|
| 1. | Diethyl ether | NS | NS |
| 2. | DCM | NS | NS |
| 3. | Acetone | S | S |
| 4. | Chloroform | NS | NS |
| 5. | Methanol | S | S |
| 6. | Hexane | NS | NS |
| 7. | Ethyl Acetate | S | S |
| 8. | Ethanol | S | S |
| 9. | Benzene | NS | NS |
| 10. | Acetonitrile | S | S |

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| | | | |
|---|---|---|---|
| 11. | Water | PS | PS |
| 12. | Acetic acid | S | S |
| 13. | DMSO | S | S |

**Table 2:** Comparative solubility of metal complexes of SAM in different solvents
S = Soluble NS = Not soluble

### 5.1.2 Solubility test of Metal Complexes of Salicylic Acid

The solubility of the metal complexes of Salicylamide is tabulated in table 3.

| S. No. | SOLVENT | Fe | Co |
|---|---|---|---|
| 1. | Diethyl ether | NS | PS |
| 2. | DCM | NS | NS |
| 3. | Acetone | S | S |
| 4. | Chloroform | NS | NS |
| 5. | Methanol | S | S |
| 6. | Hexane | NS | NS |
| 7. | Ethyl Acetate | PS | PS |
| 8. | Ethanol | S | S |
| 9. | Benzene | NS | NS |
| 10. | Acetonitrile | S | S |
| 11. | Water | PS | PS |
| 12. | Acetic acid | S | S |
| 13. | DMSO | S | S |

**Table 3:** Comparative solubility of metal complexes of SA in different solvents
S = Soluble NS = Not soluble

### 5.2 Study of Interaction of SA and SAM with Essential Metal Ion on a Silica Column

Silica is a major component of soil which acts as one of the best adsorbent. Salicylic acid, Salicylamide and essential metal ions are expected to adsorb over silica of soil. In order to check the interaction between ligand (SA/SAM) and essential metal ion, a column of metal ion adsorbed silica was set up. The ligand was then passed slowly on to the adsorbent with a flow rate of 1 ml/ minute. With a downward passage of mobile phase color of the adsorbent was changing frequently. The colored band of the column was collected in a beaker. Three types of samples are obtained of different color and their IR and UV-vis spectra were taken thereafter. After the spectral analysis it is observed that the metal complex leaches out with the mobile phase and the silica in the column shows the deviation in the peaks from the normal spectra of silica as shown in the below figures.

**IR Spectra of these samples:**

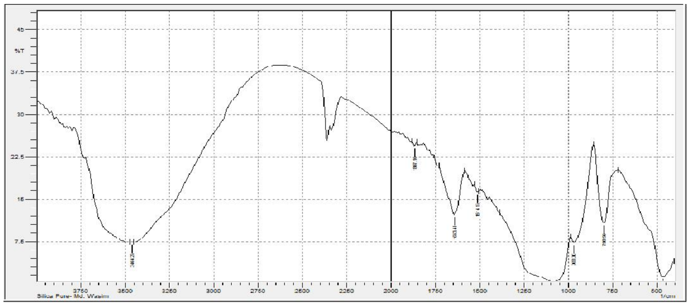

**Figure 2:** Infrared spectrum of pure silica

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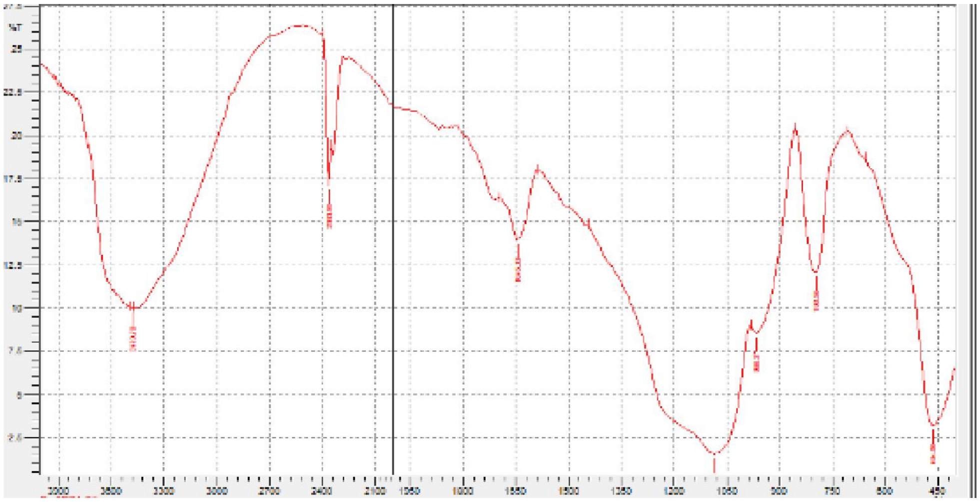

**Figure 3:** Infrared spectrum of metal adsorbed silica over SA.

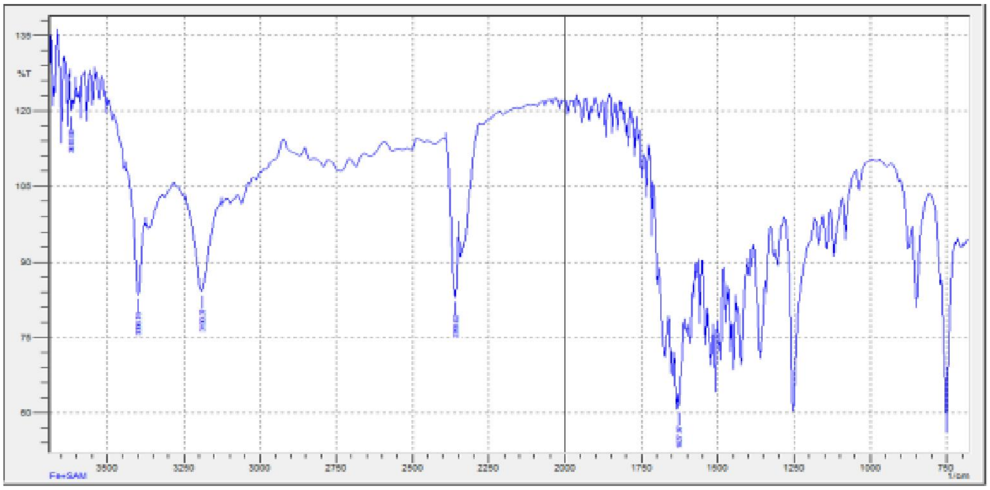

**Figure 4:** Infrared spectrum of metal adsorbed silica over SAM.

The FTIR spectra of the metal adsorbed Silica show absorption bands arising from asymmetric vibration of Si–O (1090 $cm^{-1}$), asymmetric vibration of Si–OH (950 $cm^{-1}$), and symmetric vibration of Si–O (795 $cm^{-1}$). The absorption bands between 800 and 1260 $cm^{-1}$ have been described as a superimposition of various $SiO^2$ peaks, Si–OH bonding and peaks due to residual organic groups. Water shows an intense characteristic absorption band between 3300 $cm^{-1}$ and 3500 $cm^{-1}$ assigned to O–H stretching in H-bonded water. Also this band can be cross checked through the 1635 $cm^{-1}$ band due to scissor bending vibration of molecular water. The FTIR spectra of the metal adsorbed Silica on SA and SAM shows the formation of new peaks resembling the peaks of SA and SAM).

## 5.3 Comparative study of IR of SA and SAM

The comparison table for the characterization of salicylic acid and Salicylamide is shown below. All the characteristic stretching peaks of both the compounds have obtained. During the comparison of the IR spectra of the two compounds we found big deviation in the O-H stretching frequency due to the presence of electron donating amide groups in Salicylamide, which enhances the polarity and consecutively the force constant, due to which O-H band was shifted towards the higher frequency. The weakening of C-H band maybe due to high steric hindrance due to comparatively bigger amide group that reduces the force constant between aromatic C-H. All the characteristic IR

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bands of Salicylamide have shifted towards the higher frequency because of the high steric effect of the amide group. There is an additional peak of N-H stretching of amide which is absent in case of salicylic acid. It is also observed that there is slight decrease in the O-H bending in case of Salicylamide. The major IR bands of salicylic acid and Salicylamide are tabulated below in table 6 and the IR spectra of the two are shown in figure 5 and figure 6.

| Sr. NO. | BOND | Characteristic absorptionof Salicylic acid($cm^{-1}$) | Characteristic absorption of Salicylamide ($cm^{-1}$) |
|---|---|---|---|
| 1 | O-H | 3200.41 | 3400.00 |
| 2 | O-H (bending) | 1442.69 | 1425.00 |
| 3 | C=C | 1527.05 | 1600.00 |
| 4 | C-H | 3000.15 | 3114.00 |
| 5 | C=O | 1650.41 | 1687.25 |
| 6 | N-H | No peak | 3250.00 |

**Table 4:** IR comparison table between salicylic acid and Salicylamide

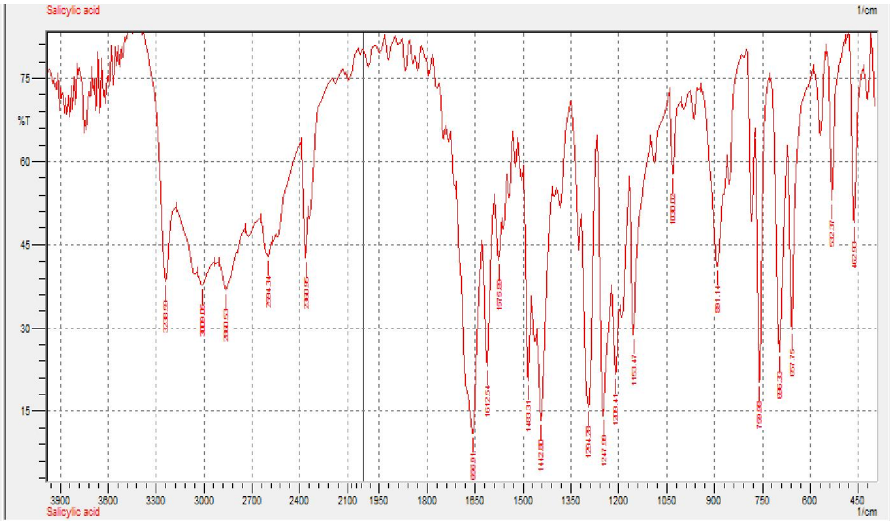

**Figure 5:** FTIR of salicylic acid

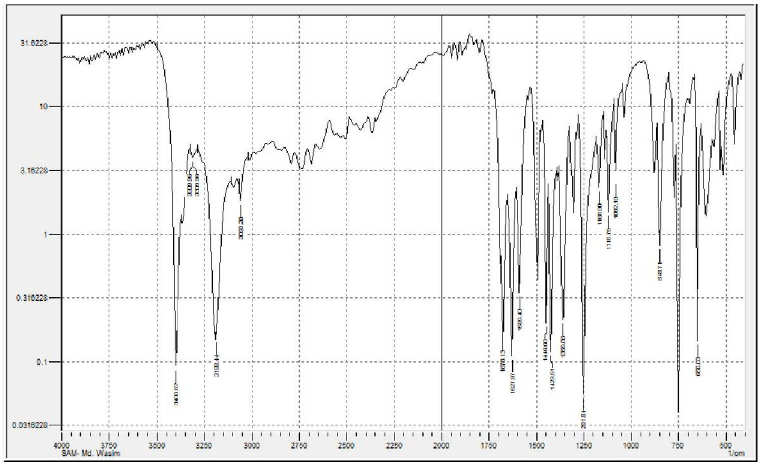

**Figure 6:** FTIR spectra of SAM

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**Characterization of metal complexes of salicylic acid and Salicylamide**

The IR spectra of the complexes are compared with that of the free ligand to determine the changes that might have taken place during the complexation; few of the spectra's are shown under as In these spectra clear change is observed in comparison to the respective Ligand which shows that the complex formation takes place.

Iron complex of SA and SAM : -IR spectra of SA and its iron complex is shown in figure 7 , while IR spectra of SAM and its iron complex is shown in figure 8 .

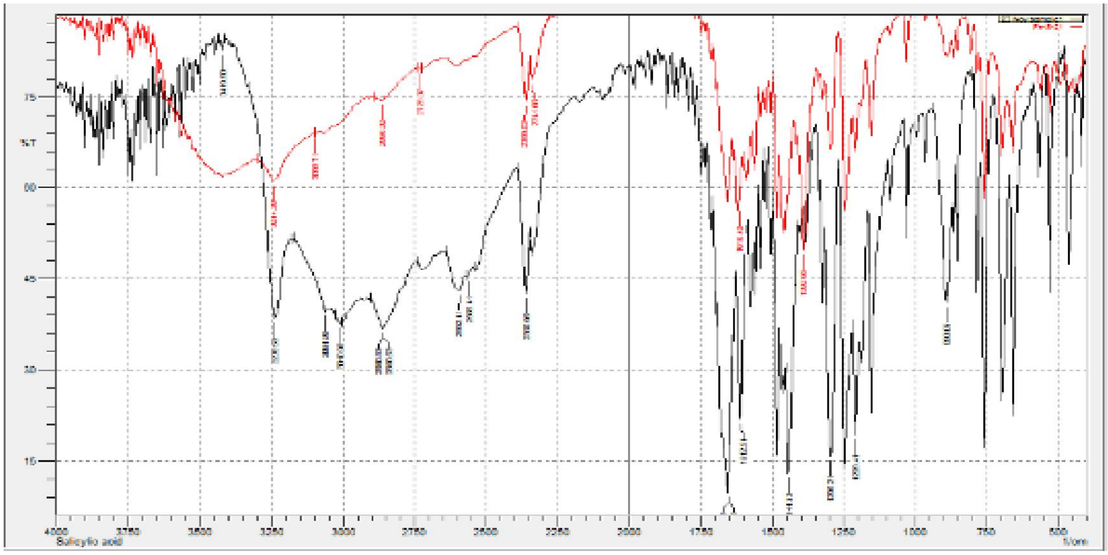

**Figure 7:** Iron complex of SA, Black one Ligand and red one is Fe + SA

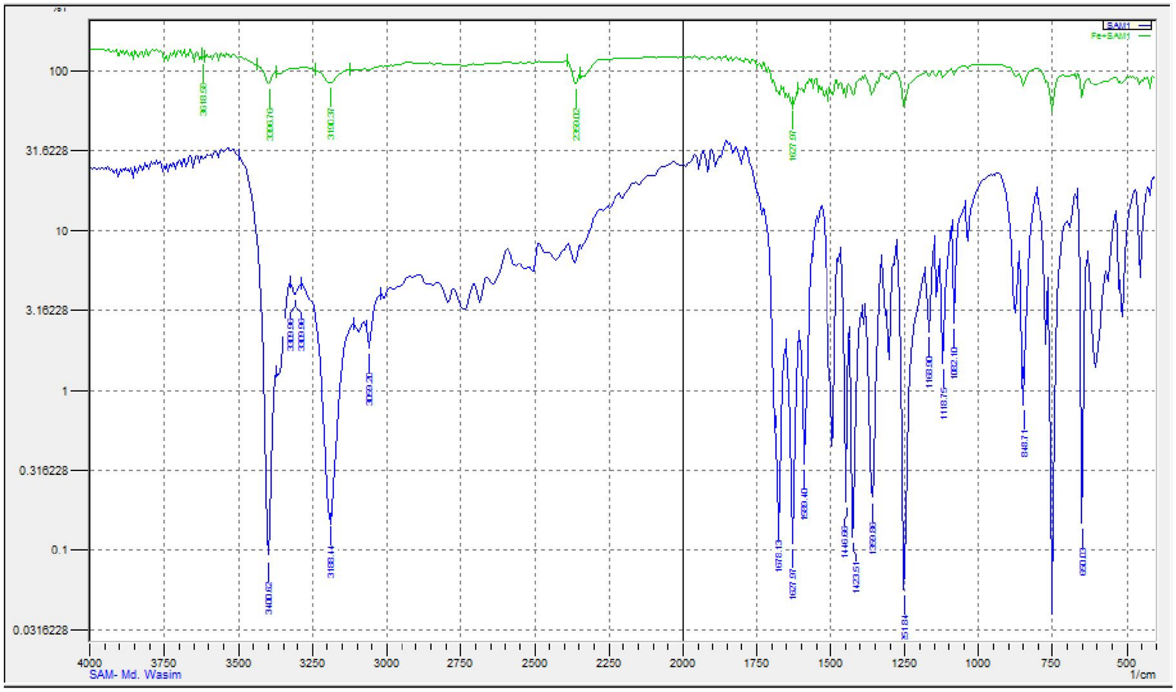

**Figure 8:** Iron complex of SAM, Blue one is Ligand and green one is of the complex formed.

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**Cobalt complex of SA and SAM**

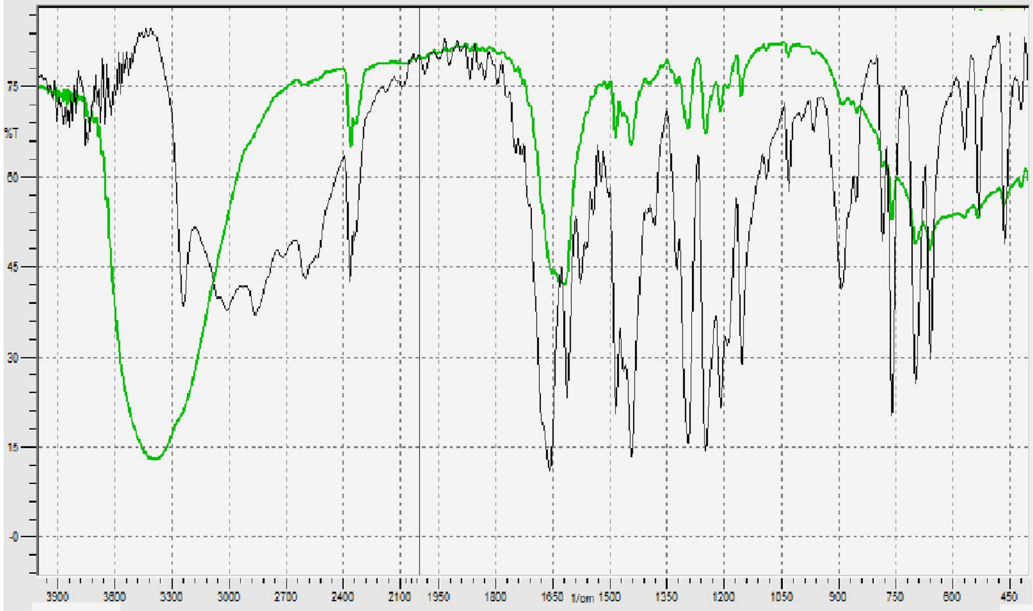

**Figure 9:** Cobalt complexes of SA, Black one is Ligand and Green one is of the complex formed.

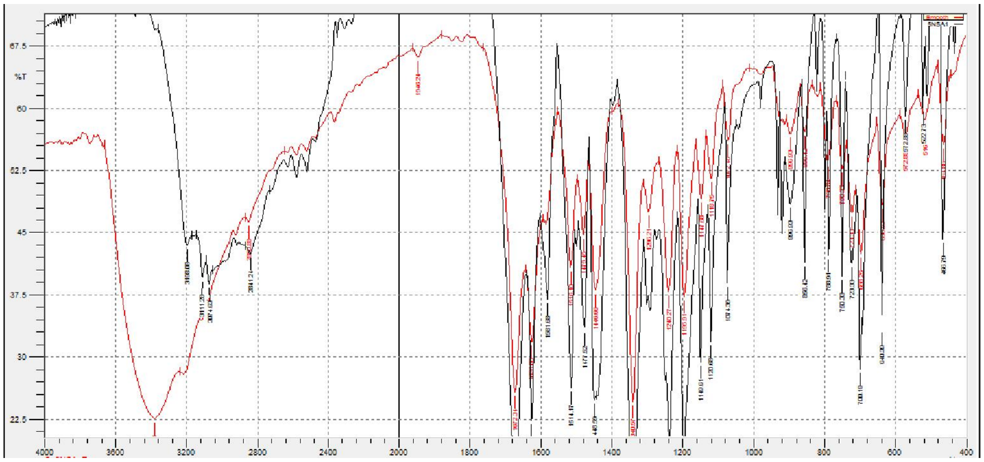

**Figure 10:** Cobalt complex of SAM Black one is Ligand and red one is of the complex formed

The IR spectra of solid SA complexes and solid SAM complexes can be divided into several regions: 3500-3000 cm$^{-1}$, the stretching absorptions of the OH-groups origination both from water molecules and from phenol groups, 2000 – 1650 cm$^{-1}$, combining vibrations, 1650-1380 cm$^{-1}$, involving both the C-O stretching of the carboxyl group and aromatic C-C stretching vibrations, 1350-1335 cm$^{-1}$, the C-O-H bending of the phenol groups, 1260 – 1230 cm$^{-1}$, stretching of the phenol group, 1200-1050 cm$^{-1}$, bending in the C-H-C plane in the substituted aromatic rings.

Following are the major shifting in the IR peaks of S A and SAM with respect to their metal complexes: there are main changes in stretching frequency of OH and C=O as shown in table 5.

| S. No. | Item | $\nu$OH (cm$^{-1}$) | $\nu$C=O (cm$^{-1}$) | Item | $\nu$OH (cm$^{-1}$) | $\nu$C=O (cm$^{-1}$) |
|---|---|---|---|---|---|---|
| 1. | SA | $3238^{m}$ | $1654^{s}$ | SAM | $3400^{m}$ | $1687^{s}$ |
| 2. | Mn-SA | $3396^{b}$ | $1620^{m}$ | Mn- SAM | $3468^{b}$ | $1623^{m}$ |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3. | Fe- SA | 3365$^{b}$ | 1624$^{m}$ | Fe- SAM | 3205$^{b}$ | 1610$^{m}$ |
| 4. | Co-SA | 3350$^{b}$ | 1621$^{m}$ | Co- SAM | 3400$^{b}$ | 1650$^{m}$ |
| 5. | Ni-SA | 3345$^{b}$ | 1615$^{m}$ | Ni- SAM | 3434$^{b}$ | 1647$^{m}$ |
| 6. | Cu-SA | 3375$^{b}$ | 1622$^{m}$ | Cu- SAM | 3432$^{b}$ | 1630$^{m}$ |
| 7. | Zn-SA | 3381$^{b}$ | 1620$^{m}$ | Zn- SAM | 3412$^{b}$ | 1635$^{m}$ |

**Table 5:** Stretching Frequency of OH and C=O of SA and SAM

s = sharp, m = medium and b = broad.

After the study of spectra of SA and SAM and their metal complexes, it is observed that a new peak (sharp) near the 3550 to 3730 cm$^{-1}$ due to free water. At 1335 to 1365 cm$^{-1}$ (medium to sharp) observed which is indicating about the carbonyl CO interaction with metal. Area from 1000 to 400 cm$^{-1}$ become broad and only few peaks i.e. M-O approximately 400 to 515 cm$^{-1}$ observed.

During the comparison of SA and its metal complexes we obtain increase in O-H bond frequency. Because in ligand SA there is intramolecular hydrogen bonding where as in metal complex there is intermolecular hydrogen bonding. C-H bond frequency is shifted to the higher frequency that indicates complexation decreases the steric hindrance of the nitro group. Both the intensity and frequency of C=O group have decreased indicating lower force constant between C=O. This is probably due to stretching of C=O bond towards the metal ion. All the bond frequencies have shifted towards lower frequency/ wave number except of C-H bond frequency and of N-H bond frequency. Increase in the N-H frequency is due to strengthening of the N=H bond because of –I effect produced by metal ion. All these IR spectra have shown between figures. Approximately small changes in C-O stretching frequency indicate that C-O stretching band was not participating in the formation of the metal complexes. The C=C stretching was shifted to higher frequency because of - I effect produced by metal ion. At the same time intensity and frequency of C=C stretching have decreased which indicate participation of C=O bond in the formation of metal complexes

### 5.4 NMR Spectroscopy

NMR of metal complex (Fe) of Salicylamide is taken. After analysis of the NMR spectra following observations are seen.

### 5.4.1 NMR of Disalicydoiron(III) chloride

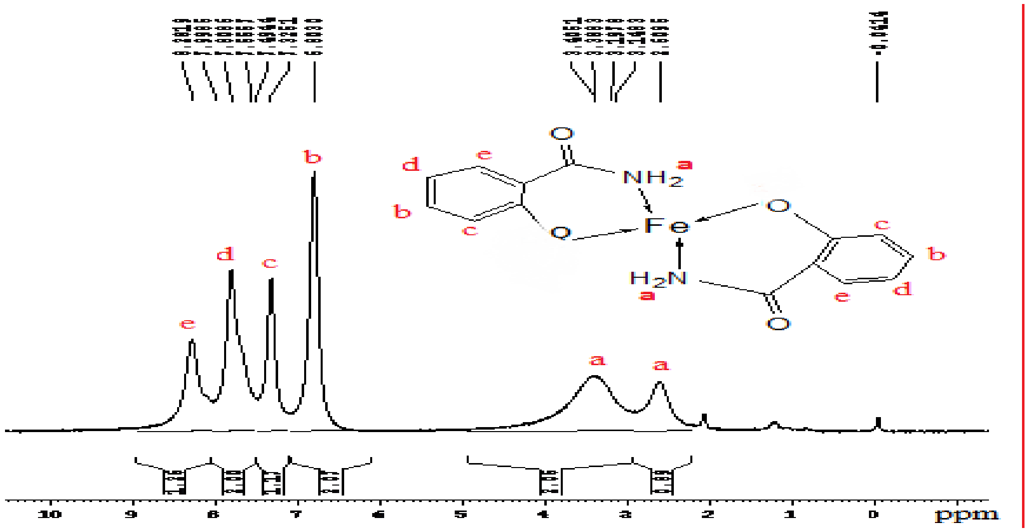

**Figure 11:** (400 MHz, DMSO); Peak at δ 2-4 p.p.m. (1H) is due to N-H proton, protons of the ring appeared at δ 4-8.5. Four different peaks of ring protons appear in the spectrum of difference in field

### 5.4.2 NMR of Disalicydocobalt(II) Chloride

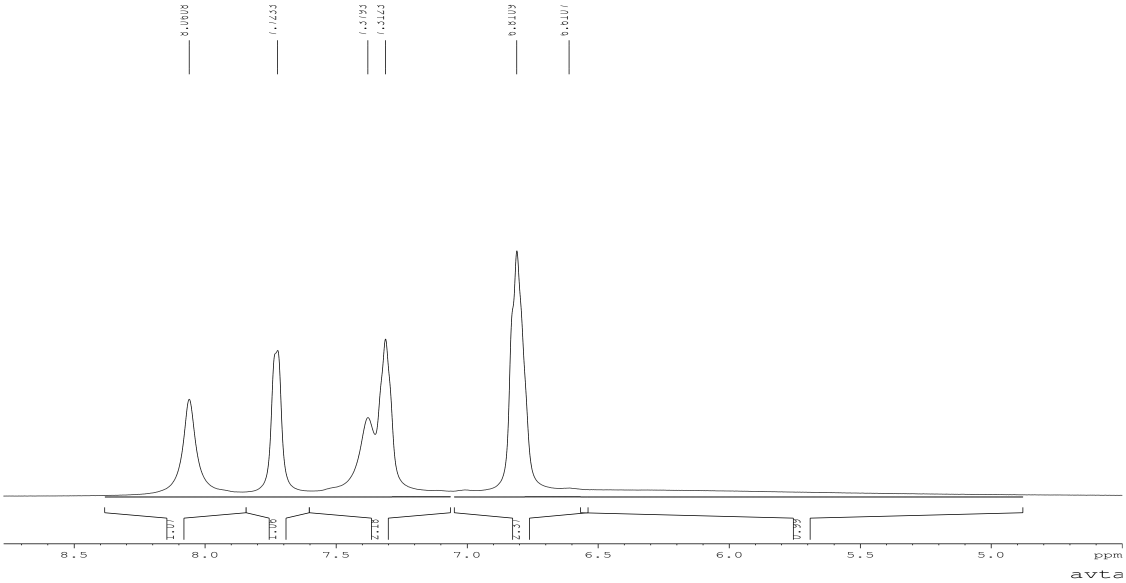

**Figure 12:** (400 MHz, DMSO); Peak at δ 2-4 p.p.m. (1H) is due to N-H proton, protons of the ring appeared at δ 4-8.5. Four different peaks of ring protons appear in the spectrum of difference in field

## VI. CONCLUSION

From the whole analysis of the salicylic acid and Salicylamide with iron and cobalt, it is concluded that SA/SAM forms the metal complexes with Co 2 and Fe 3+ . Order of complex formation is Fe 3+ &gt; Co 2+ in case of both SA and SAM. All complex formed are characterized by IR, UV-vis. The rate of interaction of metal ions with SAM was also determined using UV-visible spectrophotometer; which indicates that complexation in case of SAM take place at faster rate as compared to the SA and this occur because of the presence of amide group in SAM.

As we have discussed, that SAM is one of the derivative of salicylic acid and its derivatives associates with diverse pharmaceutical activities such as antibacterial, insecticidal, fungicidal, antimicrobial, antagonist, anthelmintic, anti-inflamonatary, etc. Beside the activities active ingredient and their metal complexes are also used as/in medicine. The extensive use of SA and probable use of SAM in near future may cause a large amount of soil pollution which in turn may cause loss of essential metal ions of soil. The target of present work is to see effect of biomedical waste (especially SA and SAM) on availability of essential metal ions of soil.

And we concluded that whenever SA/SAM are released into the environment from industrial applications, there take place complexation of metal ions with the ligand (SA/SAM) in the soil and this is check by the adsorption procedure. During this procedure, both mechanism (adsorption and leaching) takes place, and leaching take place at quite faster than the adsorption. This is confirmed by taking IR spectra and 1 HNMR of the complex formed.

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