# Synthesis and Characterization of Modified Metal Complexes of Fe (II) and Zn (II) with 2-hydroxyacetophenone azine

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***Abstract:***

2-hydroxy acetophenazine (APA) was synthesized with hydrazine hydrate and 2-hydroxyacetophenone. Bi or tridentate ligand, were formed by the 2:1 molar condensation of 2-hydroxyacetophenone with hydrazine hydrate. APA-Fe (II), Zn (II) complexes and grafted APA-Fe (II), Zn (II) complexes were synthesized and characterized by elemental analysis and infrared and electronic spectral data. APA ligand and their grafted Fe (II) and Zn (II) complexes were further identified using $^{1}$H NMR spectra and Mass spectra. The result suggests that the metal is bonded to the ligand through the oxygen and the imino nitrogen.

***Key Words*:** 2-hydroxyacetophenone azine, Grafted Metal Complexes, Characterization.

**1. Introduction:**

Recent years have a great deal of interest in the research of different types of Schiff base complexes of transition elements (l-4). The interest in the design and Synthesis of transition metal complexes containing Schiff bases lies in their biological and catalytic activity in many reactions (5-6). Many Schiff base complexes possess interesting biological properties such as antibacterial and antitumor activities (7-9). Depending on the nature of the Schiff base ligands, there are immense applications of their complexes in the chemical field. Schiff bases with variable donation sites could be monodentate, bidentate, tridentate or tetradentate forming mono or polynuclear complexes.

The term azine has two meanings in chemistry: in heterocyclic chemistry, azines are aromatic six-membered rings containing one (pyridine) to six N atoms (hexazine). In alicyclic chemistry, azines are compounds resulting from the reaction of two molecules of identical carbonyl compounds (symmetrical azines 1) or, more commonly, from the reaction of two different carbonyl compounds (unsymmetrical azines 2) with hydrazine. The compounds are called aldazines or ketazines depending on whether the carbonyl compound is an aldehyde or a ketone, respectively. There is numerous works were devoted to study the structure and vibrational spectra of Schiff base complexes [10-17] , less studies were attempted concerning the symmetric azine compounds and their complexes [18,19]. In catalysis the primary goal is to promote reactions that have high selectivity with high yields. Site isolation of the active centers by bonding to the support is a convenient method to achieve high selectivity. This procedure stabilizes the complex species and makes them act as heterogeneous solid catalysts for liquid phase oxidation [20].

For a better tomorrow, the development of eco-friendly catalysts is a challenge in front of the scientists. The catalysts should be easily separable, recyclable, and also the metal leaching from the catalyst should be nil. The pharmaceutical field is in search for catalysts for asymmetric synthesis. Moreover the poisonous effluent gases like carbon monoxide, nitrogen oxides, and sulphuroxides should be removed for a healthy and cleaner environment. Anchoring or encapsulation of inorganic complexes on various supports has been used toachieve the above mentioned goal of green chemistry.

There are several methods of supporting homogeneous catalysts, and such supported catalysts can be classified into the following categories:

I. supported liquid phase catalysts
II. Catalysts anchored on functionalized solids
III. Polymerized complexes
IV. Tethered or grafted complexes
V. Intercalated catalysts, and
VI. Encapsulated catalysts.

Of these, the present study employs the method of tethered or grafted complexes.

The earlier concept of a support was that the support is an inert substance which can provide a mean of spreading out an expensive platinum for its most effective use, or a means for improving the mechanicalstrength of an inherently; weak catalyst. However, the support material may actually contribute to the catalytic activity, depending upon the nature of reaction and conditions, and it may react to some extent with other catalyst ingredient during the manufacturing processes.

Some substance such as colloidal alumina or colloidal silica may play a double role, acting as a binding agent in catalyst manufacture and as carrier in the ultimate product.

So we have undertaken asynthesis of silica grafted 2-hydroxyacetophenone azine complexes with Fe and Zn transition metal ions [20-22]. 2-hydroxyacetophenone azines are colored compounds with potential applications in analytical chemistry The importance of the azine are due to their analogy with Schiff base considered as models of some biological systems [24, 25].

In this work, a structural study is presented for the ligand 2-hydroxy acetophenazine (APA) using UV, FTIR, NMR and Mass and for Fe(II) and Zn(II) complexes and grafted Fe(II), and Zn(II) complexes using UV, FTIR, NMR, Mass, X-ray diffraction (XRD) SEM,TEM, BET and TGA.

## 2. Experimental:

### 2.1. Materials and reagents:

All the reagents were purchased from commercial sources and used as received. Starting materials $FeCl_3 \cdot nH_2O$, $ZnCl_3 \cdot nH_2O$, 2-hydroxyacetophenone, Hydrazine hydrate were purchased from Sigma Aldrich. The solvents were purified and dried according to standard procedures [26]. All the reactions were carried out under normal conditions. The starting precursor Fe(II) and Zn(II) metal complexes were prepared according to the literature methods [27].

### 2.2 Synthesis of 2-hydroxyacetophenone Azine (Ligand):

The 2-hydroxy acetophenazine (APA) was prepared by the condensation of (0.1mol, 13.6 gm) 2-hydroxy acetophenone dissolved in 95% ethanol (100 ml) with hydrazine hydrate 90.05mol, 2.5 gm) also dissolved in 95% ethanol (50 ml) by adding the hydrazine slowly with constant stirring to 2-hydroxy acetophenone solution. The reaction mixture was heated under reflux for 1 hour. Cooling to room temperature produced yellow crystals which were filtered off under sunction and recrystallized from ethanol.

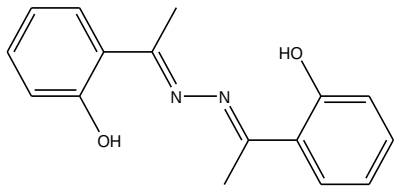



Fig.1 Structure of 2-hydroxyacetophenone azine

### 2.3 Synthesis of Metal Complex and grafted metal complexes:

The synthesized ligand was used for the synthesis of complex. Fe(II) and Zn(II) Complex was synthesized by using 1:1 metal and ligand ratio in acetonitrile. The prepared Fe and Zn complex of APA is used for synthesis of Grafted Fe and Zn complex. . Grafting on silica were carried out by using Fe and Zn complex of APA and silica in alcohol. After complete evaporation of solvent complexes get deposited on silica by hydrogen bonding between a ligand and the surface hydroxyls of silica.

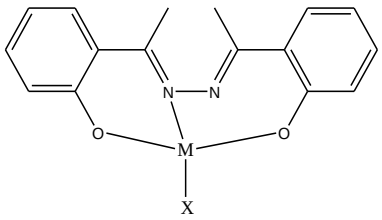



Fig.2 Structure of complexes, M= Fe, Zn and X=$H_2O$

### 2.4 Characterization:

All these metal complexes and modified metal complexes were synthesized and the pure products obtained were characterized by various analytical techniques. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer by using KBr pellets in the range of 400–4000 $cm^{-1}$. $^1H$ NMR spectra were recorded on a BrukerAvance II 400 MHz spectrometer using DMSO-$d_6$ and $CDCl_3$ as solvents. Absorption spectra were recorded on a Perkin-Elmer Lambda 25 UV–Vis spectrophotometer in the range of 200–800 nm at room temperature in acetonitrile. Elemental analyses of the complexes were performed on a Perkin-Elmer 2400 CHN/S analyzer. Mass spectra were recorded using Q-Tof APCI-MS instrument (model HAB 273). The XRD pattern obtained was recorded on a multipurpose X-ray diffractometer (Philips-1710 diffractometer with CuKα, λ = 1.5406 Å) at a scan rate of 0.17° 2θ $S^{-1}$.The field emission scanning electron microscope (FESEM) is a type of electronmicroscope that images the sample surface by scanning it with a high-energy beam ofelectrons in a raster scan pattern. Electron micrograph images were taken on a Hitachi SU 70 FESEM with a Schottky electron gun. The electrons interact with the shells in atoms thatmake up the sample producing signals that contain information about the sample'ssurface topography, composition and other properties such as electrical conductivity.The Structure and particle size

of the synthesized materials were studied using TEM with SAED on CM-200, Phillips microscope. The BET surface area was measured by $N_2$ adsorption–desorption isotherm, and was carried out on Quantachrome Autosorb Automated Gas Sorption System Autosorb-1, NOVA-1200 and Mercury PorosimeterAutosorb-1c. The thermal analysis of the complexes was carried out using a Schimadzu thermo gravimetric analyzer with a TGA-50H detector in nitrogen atmosphere. The percent weight loss was measured from the room temperature to 800 ºC at a heating rate of 10 ºC/min.

## 3. Results and discussion:

### 3.1 UV analysis of APA and its complexes:

The UV-Visible data of ligand and its complexes are summarized in Table 1. The APA exhibits three intense bands at 223 nm, 288 nm and 357 nm in acetonotrile. Comparision of APA spectra with other symmetric azines, especially salicyladazine shows that these bands can be assigned to $\pi$-$\pi^*$ ($^1$Bu← $1^1$Ag) and n-$\pi^*$ ($^1$Au ← $1^1$Ag) as for salicyladazine (18). Upon complexation, the $\pi$-$\pi^*$ transition of the ligand undergo small shift while n-$\pi^*$ one situated at higher wavelength disappears and a new main band reappears at longer wavelength (Table 1). The new strong bands at 363 and 384 nm observed for Zn-APA and Fe-APA may be assigned to LMCT transitions (2, 19).

**Table1:**Analytical data of APA, Zn-APA, Fe-APA, grafted Zn-APA, Fe-APA complexes

| Compound | Colour | % elements | | | | λ(nm) (UV/Visible) |
|---|---|---|---|---|---|---|
| | | C | H | N | M | |
| APA | Yellow | 71.45 | 6.01 | 10.44 | - | 357, 288, 223 |
| [ZnAPA($H_2O$)].2$H_2O$ | Yellow | 48.92 | 5.09 | 6.93 | 16.08 | 361, 294, 221 |
| [FeAPA($H_2O$)].2$H_2O$ | Yellowish green | 50.45 | 5.22 | 7.27 | 15.34 | 384, 297, 230 |

### 3.2 Analysis of IR of APA and its complexes:

The IR spectra in the range 4000-400 $cm^{-1}$ of APA complex are shown in Fig. 3 as an example. The assignment of APA and the two studied complexes are reported in Table 2. The vibrational assignment of chelates spectra and structure will be discussed.

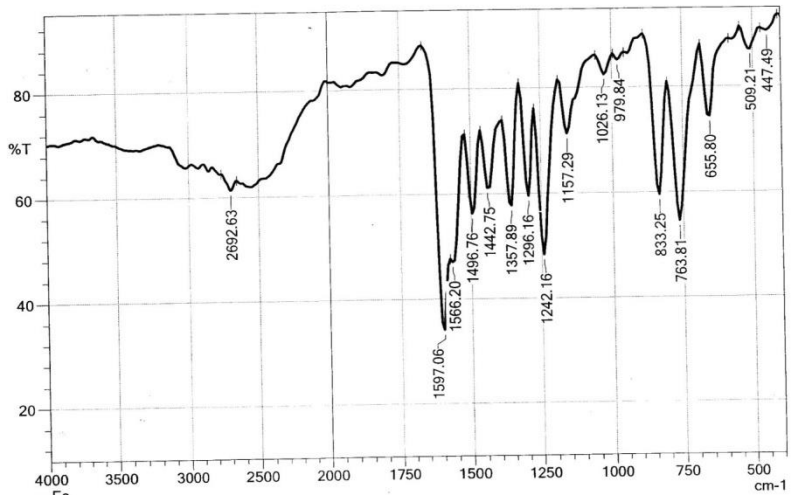



Fig.3 The FTIR spectra of Fe-APA complex

Table 3 FTIR spectra of APA and its complexes

| APA | Fe-APA complex | Zn-APA complex | Assignment |
|---|---|---|---|
| 2630 $cm^{-1}$ | 2692$cm^{-1}$ | 2681$cm^{-1}$ | υ= OH ($H_2O$) |
| 1587$cm^{-1}$ | 1597$cm^{-1}$ | 1599$cm^{-1}$ | υ= C=N |

The υ OH stretch of the hydroxyl group of the ligand at 2630 $cm^{-1}$ disappears and a new band arises at 2692$cm^{-1}$ and 2681 $cm^{-1}$ which can be assignes to OH of the water molecule for the Fe-APA and Zn-APA complexes. The υ of C=N of Fe-APA and Zn-APA shifts to higher wave number (Table 3). This indicates that the ligand is coordinated through its imine group(1,3 11,12).The Fe-APA and Zn-APA complexes are characterized by a new strong band at 1597$cm^{-1}$ and 1599 $cm^{-1}$ respectively. Finally new IR band observed at 504 $cm^{-1}$and 506 $cm^{-1}$are assigns to the υ M-O stretch of Fe-APA and Zn-APA respectively.

### 3.3 NMR analysis of APA and its complexes:

The structures of the Azine, Fe and Zn-Complex were confirmed by their spectral analysis. The $^1H$ NMR spectrum of compound Azine Fe and Zn Complex in $CDCl_3$ clearly shows total eight aromatic protons. The Eight aromatic protons of aromatic ring appeared at δ 6.8 to 7.8 (Fig. 4). It also shows the presence of OH proton at 12.8 δ.

### 3.4 Mass of APA and its complexes:

The molecular weight of ligand APA and Fe-APA and Zn-APA complex is well matches with the m/e peak in mass spectrum (fig.5) which confirms the formation of complexes.

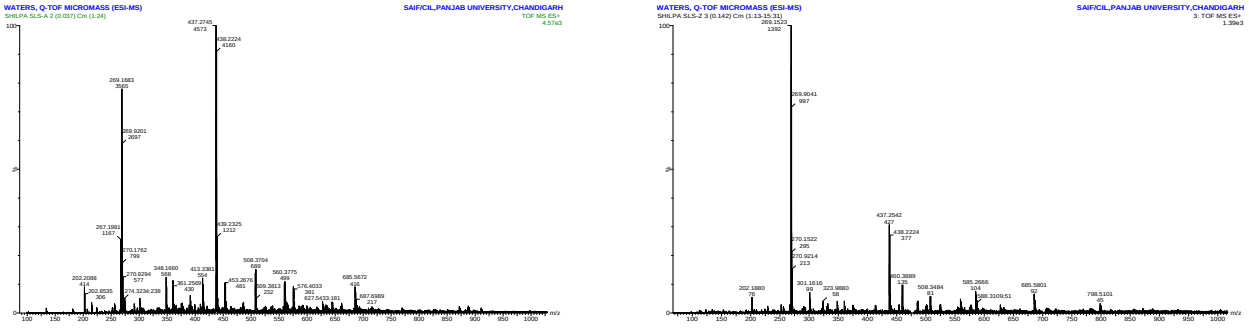



**Figure 5:** Mass analysis of ligand APA and Zn complex

### 3.5 The X-ray structural characterization:

The XRD pattern of the complex and silica grafted complex are shown in fig. 6. The XRD pattern of Schiff base Fe-complex, grafted Fe complex in fig.6a and Zn-Complex, grafted Zn complex was shown in Fig. 6b. The x-ray diffractogram of Fe- complex was scanned in the range 0-80° at wavelength 1.543 Å. The diffractogram and associated data depict the 2θ value for each peak, relative intensity and interplanar spacing (d-values). The x-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10% has been indexed by using computer programme. The above indexing method also yields Miller indices (hkl), unit cell parameters and unit cell volume. Hence it can be concluded that Fe and Zn-complex has crystalline structure and Silica grafted Fe and Zn-complex has amorphous structure.

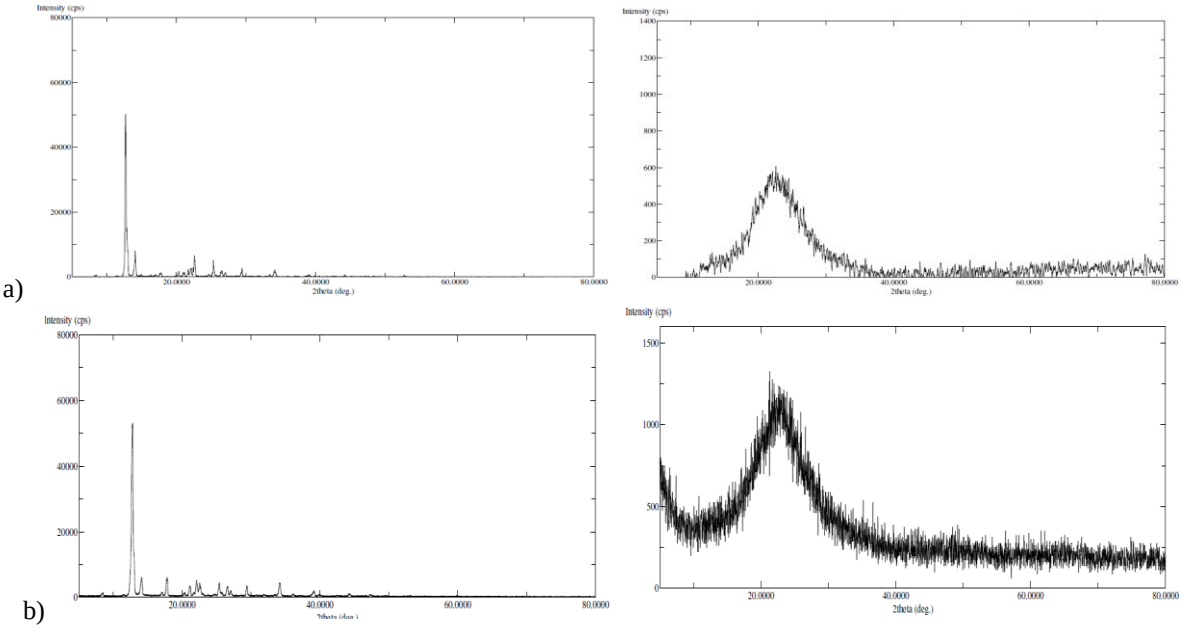



**Figure 6:** XRD Spectra for a) Fe-complex, Grafted Fe-complex and b) Zn-Complex, grafted Zn-Complex

### 3.6 SEM, TEM and SAED pattern of complexes:

Figure 7 shows surface morphology of Fe-complex and Zn-Complex by SEM coupled with EDAX. The SEM shows that the particles are agglomerated with each other. The EDAX data furnishes elemental composition in conformity with respective molar proportion taken.

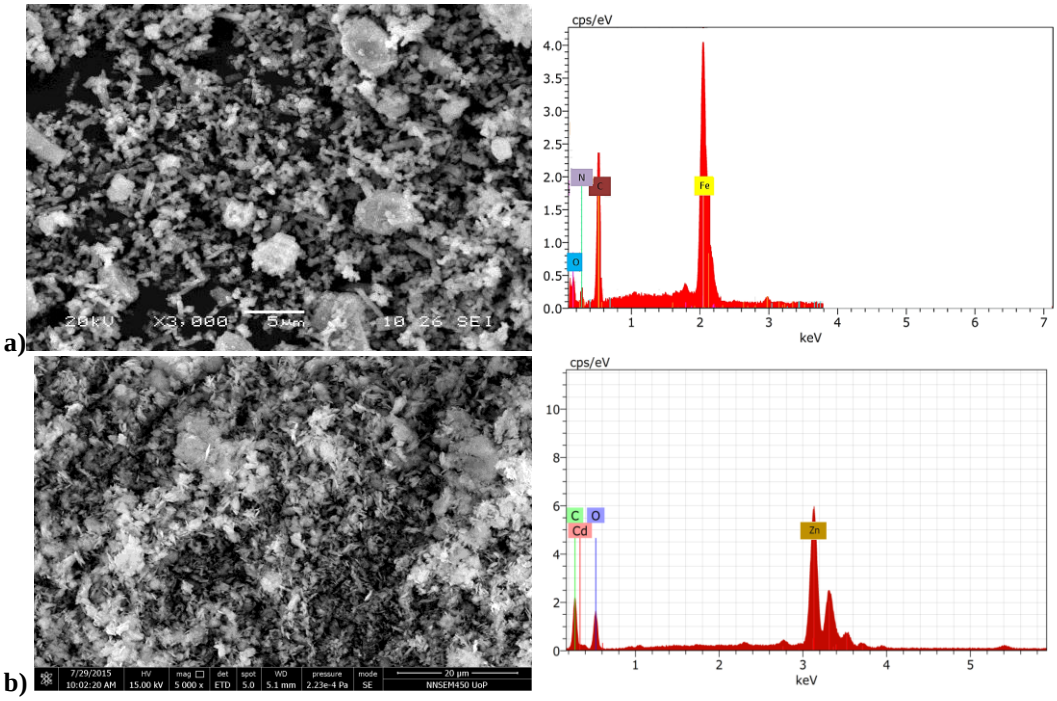



**Figure 7:** SEM and EDS analysis of a)Fe-Complex and b) Zn-complex

The TEM image (Fig. 8a-b) of grated Fe and Zn-complex shows some crystals are cubic and rod like. The SAED pattern associated with TEM reveals that Fe-Complex and Zn complex structure and is in total agreement with XRD data.

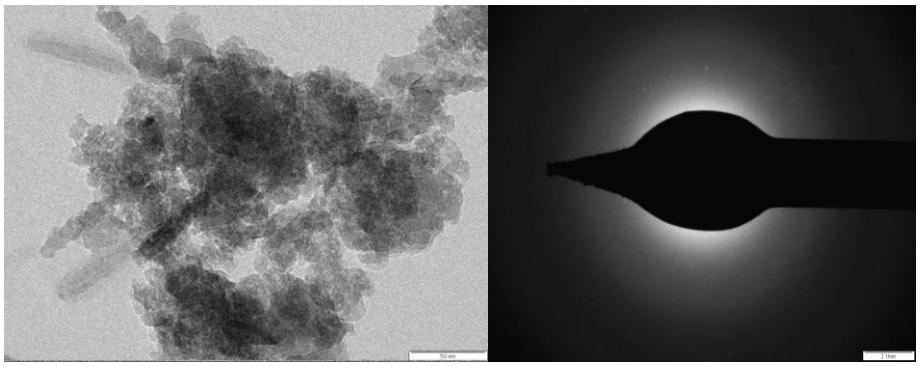


**Figure 8a:** TEM and SAED analysis of grafted Fe-Complex

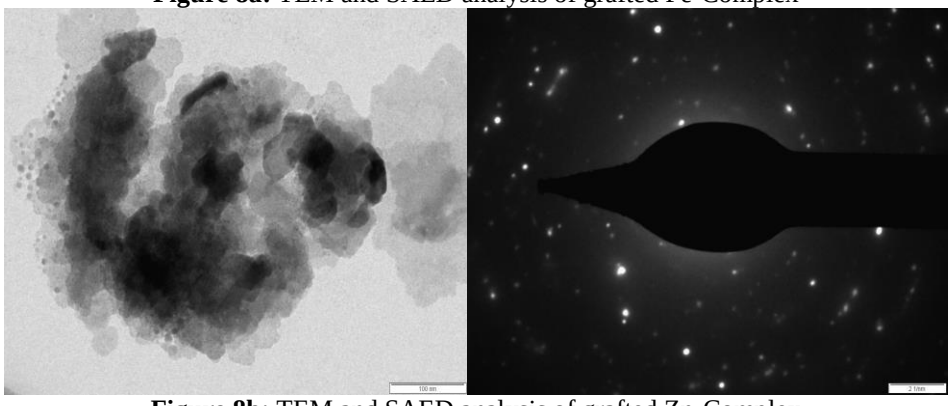
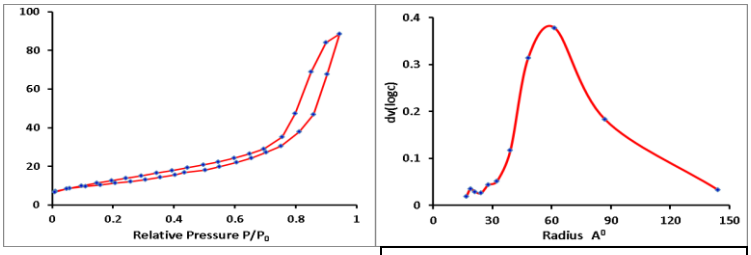


**Figure 8b:** TEM and SAED analysis of grafted Zn-Complex

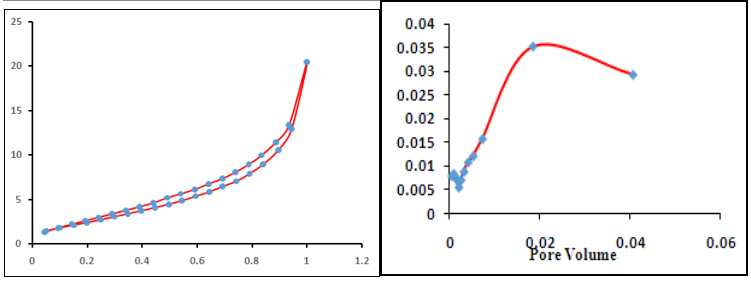
**3.7 BET analysis of complexes:**

Figure 9(a, b) shows the $N_2$ adsorption-desorption isotherms and the BJH pore size distribution of synthesized grafted Fe and Zn-Complex. It reveals that all the samples have typical IV $N_2$ adsorption-desorption isotherms with $H_1$ hysteresis which indicates that the samples reserve the cylindrical mesoporous. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Based on the $N_2$ adsorption-desorption isotherms, Fe-complex has surface area ($S_{BET}$) is 178.9 $m^2/g$, the average pore volume (Vp) and pore diameter (dp) were 0.105 cc/g and 54.37 $A^0$.While Zn-complex has surface area ($S_{BET}$) is 134.32 $m^2/g$, the average pore volume (Vp) and pore diameter (dp) were 0.023 cc/g and 26.67 $A^0$ respectively.

a)




b)




**3.8 The thermal analysis of complexes:**

The thermogram of Fe-APA complex shows that there is two water molecules as water of coordination, the decomposition range was (110-180ºC) and two water molecules involved as hydration water in the range (74-105 ºC). The initial mass loss observed for Zn-APA complex in the temperature range (80-120ºC) corresponds to two water molecules attributed as water of hydration. In the temperature range (180-210 ºC) the mass loss shows the presence of one coordinated water molecules.

**Conclusion:**

Hence based on the elemental analyses UV/visible, FTIR, NMR, Mass spectra and TGA one may propose that the ligand is coordinated with the two metal ions Fe(II) and Zn(II) through the two oxygen atoms, one of the nitrogen atom of the imine group and one water molecule (Fig.2). On the basis of XRD, SEM, EDAX, TEM and BET analysis complexes are grafted on silica and can be used as a catalyst in organic synthesis.

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