



SYNTHESIS AND SPECTRAL CHARACTERIZATION OF MANGANESE (II) AND IRON (III) WITH DITHIOCARBAMATES

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Abstract : Synthesis of new dithiocarbamates namely AMPDTC derived from 2-amino-6-methyl pyridine and Carbon disulphide. 2-amino-6-methyl pyridine is one of the important compounds of unique series of amino pyridine. The main interest is to prepare the new dithiocarbamate metals [AMPDTC] complexes with Mn and Fe metals. Dithiocarbamate have been synthesized and characterized on the basis of elemental analysis, IR, ¹HNMR spectra, X-ray powder diffraction and TGA- DTA studies. The infrared and ¹HNMR data have shown that the ligands behave as isobidentate ones. The electronic spectra show that mostly ligand centered charge transfer transitions occur. In thermal studies, interesting fragmentation patterns are reported and kinetic parameters such as order of the thermal radiations (n) and activation energy *E* have also been evaluated.

Keywords: Dithiocarbamates, Metal complexes, Biological activity

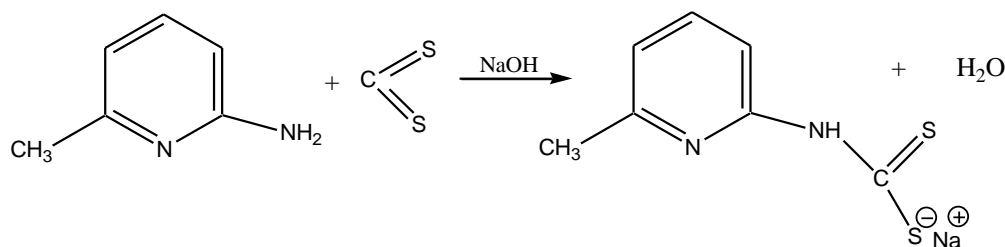
Introduction: The spectacular importance of dithiocarbamate ligands lies in the formation of complexes with metal ions. This is due to the presence of lone pair of electron donating character. They also form five or six membered stable chelates with metals^{1,2}. Besides the ability to form complexes with metal ions, dithiocarbamates have innumerable applications in many fields namely, Pharmacy, medicine, agriculture, photography and polymer technology. In Biological view these are applicable as antiviral, antibacterial and anticancer activities. Literature survey revealed that many number of dithiocarbamates have been synthesized from Primary and secondary amines. The proposal work based on the synthesis of new dithiocarbamates namely AMPDTC derived from 2-amino-6-methyl pyridine and Carbon disulphide. 2-amino-6-methyl pyridine is one of the important compounds of unique series of amino pyridine. The main interest is to prepare the new dithiocarbamate metals [AMPDTC] complexes with Mn and Fe metals. Further extended the antibacterial activity of synthesized dithiocarbamate ligand and its metal complexes by Paper disc method through microorganisms such as E.Coli, Bacillus subtilis & Klebsiella.

Materials and Methods:

Analytical reagent grade chemicals were used in the present research work. Organic compounds are 2-Amino-6-methyl Pyridine (HiMedia), Carbon disulphide (Qualigens) and Methanol (AR-Loba). Inorganic compounds are Manganese Chloride (SD Fine), Ferric chloride (Sigma Aldrich), Sodium acetate trihydrate (AR-Merck) and Sodium Hydroxide (SD Fine).

Preparation of ligand:

The cold methanolic solution of 2-Amino-6-methyl pyridine (0.51gm in 10 cm³) is transfer into the clean casserole; add 5ml of 5N NaOH solution. To this mixture gradually add Carbon disulphide (8ml) drop wise over a period of 30 minutes with constant stirring, oily precipitate separates out. The white precipitate formed was allowed to stand for 5 hours in the water bath for crystallization. The product was filtered on a Buchner funnel through suction, washed with Methanol and sucked dry. The product thus obtained was recrystallized from ether and dried in vacuum over calcium chloride dessicator. Yield is 80% and Melting Point is 195 - 197⁰ C. The new dithiocarbamate is,



Preparation of Manganese (II) and Iron (III) metal complexes:

Metal complexes were prepared by adding adequate amount of dithiocarbamate ligand in 50% Methanol to metal salt solution of Mn and Fe metal ions in the presence of sodium acetate and reflux the mixture for four hours on a water bath. This reaction mixture was poured in excess of cold water. A coloured precipitate of metal complex was obtained with good yield. These products were washed several times with hot water and cold methanol to free them from unreacted metal salt and ligand respectively and finally with ether and dried in a vacuum dessicator. Samples of high purity were obtained directly. The purity was also checked by TLC.

The elemental analyses for both the ligands and complexes were carried out by an elemental analyzer. The metal contents were determined by atomic absorption spectroscopy after digesting the complexes with conc. HNO_3 . Conductivity measurement's were carried out with a Beclanan Re-18A type conductivity bridge for freshly prepared 10 M solutions in DMF at $300 \pm 0.1^\circ\text{K}$. Room temperature magnetic susceptibility measurements were made by using the Guoy method.

The Infrared spectra were recorded with a Perkin-Elmer IR 598 Spectrometer ($4000\text{--}200\text{cm}^{-1}$) using KBr pellets in the range. ^1H NMR spectra were recorded on an av-300 MHz NMR spectrometer in DMSO-d_6 solvent at room temperature. The TG and DTA curves were simultaneously recorded for powdered samples on a IUGAKU 8150 thermoanalyser at the heating rate of $10^\circ\text{K min}^{-1}$ and the chart speed was maintained at 2.5 min^{-1} as the reference material. The X-ray powder diffraction patterns were obtained on a Lynx-Eye Detector, Make: Burker Axs, Model:D8 Advance.

Results and Discussion:

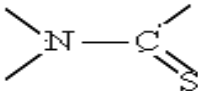
Characterization of the ligand:

Elemental analysis revealed that the percentage composition of carbon, hydrogen, nitrogen and sulphur were in good agreement with theoretically computed values.

IR spectrum of the compound clearly revealed that the formation of dithiocarbamate has taken place and the peak at $1500\text{--}1450\text{ cm}^{-1}$ shows the existence of Thioureide band $\text{>N}-\text{C}(=\text{S})_2$ in the compound. The peak at 1459 cm^{-1} assignable to $\nu(\text{N-CSS})$ stretching frequency, this band define a carbon, nitrogen bond order between a single bond ($\nu=1250\text{--}1350\text{ cm}^{-1}$) and a double bond ($\nu=1640\text{--}1690\text{ cm}^{-1}$). The appearance of a band in that region indicates that, the strong delocalization of electrons in the dithiocarbamate moiety. The above peaks of dithiocarbamate shows good agreement with reported literature for thioureide band. The peak at 1616 cm^{-1} is observed which is characteristic of (>C=N) of the pyridine ring.

Analytical data and spectral data of Sodium 2-amino-6-methyl pyridine dithiocarbamate is given in the Table-1

Table-1 Analytical and Spectral data of AMPDTC

Molecular Formulae	C ₇ H ₇ N ₂ S ₂ Na	
Colour	Colour less	
Melting Point	195-197 ⁰ C	
Elementary Analysis	Found (%)	Caliculated(%)
Carbon	40.05	40.76
Hydrogen	3.00	3.42
Nitrogen	13.00	13.58
Sulphur	31.30	31.90
Yield	80 %	
I.R Absorption Bands		
	1460 cm ⁻¹ , 770 cm ⁻¹ , 1130 cm ⁻¹	

INFRARED SPECTRAL STUDIES:

A plot of IR spectra shows the frequency or wave number of incident radiation on the X-axis and its transmittance on the Y-axis. The wave number unit is often used, since it is directly proportional to the energy of vibration and as such modern IR instruments are linear in cm^{-1} scale. It was observed that the IR spectra of all the Manganese (II), and Iron (III) ion complexes gave a considerable number of peaks, each corresponding to a particular vibrational transition.

Table.2., depicts the analysis of IR spectrum of the ligand and metal complexes of Mn and Fe. The typical IR spectrum are shown in Fig 1,2 & 3.

I.R. Analysis of the Ligand

The typical I.R spectra of AMPDTC ligand is presented in the Fig 1. As concern the 2-Amino-6-methyl pyridine dithiocarbamate moiety, two main regions of the IR are of main interest. First, the $(1420-1490 \text{ cm}^{-1})$ region, which is primarily associated with ν (N-CSS) stretching vibrations. Second, the 769 cm^{-1} region, which is associated with ν (C-S) stretching vibrations, the weak band is in the 1130 cm^{-1} region and is associated with the $\nu(\text{C}=\text{S})$ stretching vibrations.

The characteristic band at 1473 cm^{-1} , is assignable to ν (N-CSS); this band defines a carbon Nitrogen bond order between a single bond ($\nu = 1250-1350 \text{ cm}^{-1}$) and a double bond ($\nu = 1600-1700 \text{ cm}^{-1}$). The appearance of a band in that region indicates that, of the three possible resonance structures reported by Chatt et al., characterized by a strong delocalization of electrons in the dithiocarbamate moiety.

The band at $3200-3250 \text{ cm}^{-1}$ associated with the ν (N-H) stretching vibrations and the band at $1550-1590 \text{ cm}^{-1}$, is associated with the $\nu(\text{N}=\text{C})$ bond stretching in the Pyridine ring.

The bands at $2910-2930 \text{ cm}^{-1}$ and $1330-1380 \text{ cm}^{-1}$, are associated with the ν (C-H) stretching vibrations and δ (C-H) bending vibrations of Methyl group which is attached to the Pyridine ring in 6th position.

I.R. Characterization of Mn (II) Complex:

The interpretation of IR spectra of dithiocarbamate complexes of Transition metals has arisen considerable interest both diagnostically to determine the mode of co-ordination and as a mean of assessing the nature of bonding in these complexes. The Infrared spectrum of the [AMPDTC] ligand is compared with the Mn(II) complex. The typical I.R spectra of [AMPDTC] Mn ligand is presented in the Fig 2.

A strong band exhibited at 1460 cm^{-1} in the I.R spectrum of the ligand, which is assigned to the Thioureide bond is shifted to 1575 cm^{-1} region. On Passage from the free dithiocarbamate ligand to their complex, the ν (N-CSS) mode is shifted to higher energies, showing an increase of Carbon-Nitrogen double bond character and hence a greater contribution of the structure $\text{—N}=\text{C}=\text{S}(\text{—})$. The Infrared active ν (N-CSS) mode is sensitive to both chain length and the steric bulk of the substituents. As double character is more pronounced in the complex it can be concluded that the ligand is co-ordinated via S,S atoms.

To discern the bonding type of the dithiocarbamate ligand in their complexes, the Bonati-Ugo method is, by far, the most popular one. It consists of tracing the $950-1060 \text{ cm}^{-1}$ spectral region, where the ν (C-S) modes are thought to appear. In fact, the bands due to —CSS moiety is usually coupled to other vibrations and are very sensitive to the environment around this group, but they are also useful to distinguish between Monodentate and Bidentate Co-ordination. The presence of only one band in the investigated region, commonly attributed to ν (SCS) mode, it indicates completely symmetrical bonding of the dithiocarbamate ligand to Metal in bidentate mode, where as a doublet is expected for the Monodentate co-ordination.

Basing on the above concept the presence of single band at $980-1030 \text{ cm}^{-1}$ region is assumed to ν (C-S) stretching vibrational mode and it indicates the symmetric bidentate behaviour of the ligand that means the AMPDTC ligand is co-ordinated via both the sulphur atoms.

Along with these bands new bands are formed which are not observed in the spectra of the ligand, the band at 450 cm^{-1} is assigned to the ν (Mn-S) metal ligand bond of the complex. The appearance of a broad band at 3442 cm^{-1} can be assigned to the ν (O-H) stretching vibrations of co-ordinated water molecules present in the complex and the band at 1575 cm^{-1} due to ν (C=N) of the pyridine ring does not show any considerable change in the complex, which indicates that the pyridine Nitrogens is not participating in the complex formation. In the spectra of both ligand and complex, no significant change is observed, for ν (N-H) stretching mode, indicating non-involvement of amino nitrogen in Co-ordination. The two weaker bands at $800-750 \text{ cm}^{-1}$ and $750-720 \text{ cm}^{-1}$ are assigned respectively to -OH rocking and wagging vibrations of co-ordinated water in the complex.

I.R Analysis of Fe (III) Complex:-

The Infrared spectrum of the [AMPDTC] ligand is compared with the Fe(III) complex. The typical I.R spectra of [AMPDTC] Fe ligand is presented in the Fig 3.

A strong band exhibited at 1473 cm^{-1} in the I.R spectrum of the ligand, which is assigned to the Thioureide bond is shifted to 1530 cm^{-1} region. This shift to higher wave number supports considerable double character of the (N-CSS) bond^{3,4,5}. As double character is more pronounced in the complex it can be concluded that the ligand is co-ordinated via S,S atoms, and this is supported by the canonical forms given by Chatt et al. The presence of a single strong band at $950-1060 \text{ cm}^{-1}$ region is assigned to ν (C-S) stretching vibrational mode. The ν (C=S) bands at 1156 cm^{-1} and ν (C-S) bands at 769 cm^{-1} in the ligand shows negative and positive shift, respectively in the spectra of the complex indicating the co-ordination of both S-atoms. This indicates the bidentate behaviour of the AMPDTC ligand in the complex, other wise a doublet would be expected in the $950-1060 \text{ cm}^{-1}$ region as in the case of Monodentate co-ordination. Along with these bands new bands are formed which are not observed in the spectra of the ligand, the band at 410 cm^{-1} is assigned to the ν (Fe-S) metal ligand bond of the complex. The appearance of a broad band at 3438 cm^{-1} can be assigned to the ν (O-H) stretching vibrations of co-ordinated water molecules present in the complex and the band at $1550-1570 \text{ cm}^{-1}$ due to ν (C=N) of the pyridine ring does not show considerable change in the complex which indicates that the pyridine Nitrogen is not participating in the complex formation. In the spectra of both ligand and complex, no significant change is observed, for ν (N-H) stretching mode, indicates the non-involvement of amino nitrogen in Co-ordination.

The band recorded for both the complexes and free dithiocarbamate precursors in the 410-630 cm^{-1} range can be ascribed to the contribution of $\nu(\text{C-S}) + \delta(\text{SCS})$ vibrational modes. The two weaker bands at 800-750 cm^{-1} and 750-720 cm^{-1} are assigned respectively to -OH rocking and wagging vibrations of co-ordinated water in the complex.

Table 2. The important IR Bands of the Ligand and Their Metal Complexes

Compound	OH (water)	$\nu(\text{C-N})$ (Thioureide bond)	$\nu(\text{C-S})$	$\nu(\text{M-S})$
AMPDTC	-	1473	1130,789	-
(AMPDTC) ₂ Mn	3442	1575	975	420
(AMPDTC) ₂ Fe	3438	1530	990	412

COMPLEX STUDIES of ^1H NUCLEAR MAGNETIC RESONANCE SPECTRA

In the present study, ^1H NMR spectra were recorded on an av-300 MHz NMR spectrometer in Apotex Pharma chem..India pvt. Limited Bangalor in DMSO- d_6 solvent at room temperature.

Analysis of AMPDTC and its Metal complexes

Fig. 4,5 & 6. Depict the noted the important chemical shift values of the ligand and metal complexes, these values are summarized in Table.3.

Fig.4. gives the typical NMR spectrum of the ligand AMPDTC. The methyl protons of the picoline of dithiocarbamate ligand were observed at 2.60-3.60 ppm. The peaks in the aromatic region were seen as a set of multiplets in the range 6.6-7.6 ppm^{6,7,8} and the signal due to proton attached to the Nitrogen, in thioureide bond is appeared as a singlet at 7.4 ppm.

Fig.5. gives the typical NMR spectrum of the [AMPDTC]Mn. In the complex [AMPDTC] Mn the signal due to proton bonded to Nitrogen in thioureide bond is shifted from 7.34 to 7.85 ppm in the case of the ligand. The down field shift of the complex may attributed to an increase of the π - bond character and the delocalization of electron along the C-N bond contributed by the substituents and also the bidentate nature of the dithiocarbamate ligand. On complexation, the electron density on -NH decreases, the precessional frequency of Nitrogen containing proton increases, hence the signal is shifted to down field regions.

It was observed that the aromatic ring protons of range 6.74-7.45 ppm become broad and less intensive when compared to the corresponding dithiocarbamate ligand. This effect may be due to the drifting of ring electrons towards the metal ion.

The broad signal at 9.8 ppm in the case of Manganese(II) complex indicates the complexation of water molecule to metal ion.

Fig.6. gives the typical NMR spectrum of the [AMPDTC] Fe. In the complex [AMPDTC] Fe the signal due to the nitrogen containing proton is shifted from 7.34 to 7.81 ppm in the case of the ligand. The down field shift of the complex may attributed to an increase of the π -bond character or the delocalization of electron along the C-N bond contributed by the substituents and also the bidentate nature of the dithiocarbamate ligand.

It was observed that the aromatic ring protons of range 6.6-7.6 ppm become broad and less intensive when compared to the corresponding dithiocarbamate ligand². This effect may be due to the drifting of ring electrons towards the metal ion.

The broad signal at 10.1 ppm in the case of Iron (III) complex indicates the complexation of water molecule to metal ion.

Table.3. ^1H NMR Spectrum of the ligands and its metal complexes in DMSO- d_6 in ppm

Compound	H-N-C (thiureide bond)	CH_3	OH	Ar-H
AMPDTC	7.34	2.60	-	6.6-7.6
(AMPDTC) ₂ Mn	7.65	2.54	9.8	7.45-8.2
(AMPDTC) ₂ Fe	7.89	2.51	10.1	5.42-6.4

ESR Studies of coordination complexes:

The ESR spectral studies are carried only for Mn [AMPDTC] complex. Because of the fact that the Spin-Orbit coupling constants for the 4d and 5d groups are much larger than for the 3d group, Spin-lattice relaxation times are usually very low. Thus it is often difficult to observe a spectrum at all except at very low temperatures.

The structures of complex in solution may be different from those present in the solid state. In solution the ESR spectrum will be different due to the increase in separation between Mn-Mn for tumbling motion of Iron species in the solution. The ESR spectra were obtained in solution for all Iron complexes in DMF medium at liquid nitrogen temperature.

The ESR spectra of the complex in polycrystalline state exhibit only one broad signal, which is attributed to dipolar broadening and enhanced spin - lattice relaxation³⁶³. ESR spectra obtained for copper complex in DMF at liquid nitrogen temperature and representative ESR spectrum of Mn (II) ion complex are presented in Fig.7. In this low temperature spectrum, four peaks of small intensity have been identified which are considered to originate from g_{\parallel} component.

The spin Hamiltonian, orbital reduction and bonding parameters of the complex were given in Table.4. The g_{\parallel} and g_{\perp} are computed from the spectrum using DPPH free radical as g marker. Kivelson & Neiman have reported that g_{\parallel} value is less than 2.3 for covalent character and it is greater than 2.3 for ionic character of the metal- ligand bond in complex. Applying this criterion, the covalent bond character can be predicted to exist between the metal and the ligand for complex³⁶⁶.

The trend $g_{\parallel} > g_{\text{ave}} > g_{\perp} > 2.0023$ observed for the complex suggests that the unpaired electron is localized in $\text{dx}^2 - \text{y}^2$ orbital³⁶⁷ of the Mn (II) complex. The lowest g value (>2.04) also consistent with a $\text{dx}^2 - \text{y}^2$ ground state. It was observed that the G value for the Cu-complex was less than four and suggests that there are no interactions between copper - copper centres in DMF medium.

The ESR parameters g_{\parallel} , g_{\perp} , A_{\parallel}^* , and A_{\perp}^* of the complex and the energies of d-d transitions are used to evaluate the orbital reduction parameters (K_{\parallel} , K_{\perp}), the bonding parameters (α^2), the dipolar interaction (P) and the Fermi constant interaction term (K)³⁶⁸. The observed $K_{\parallel} < K_{\perp}$ indicates the presence of significant in plane π -bonding. The α^2 values for the present chelate 0.4109 supporting the covalent nature of the complex. Giordano and Bereman suggested the identification of bonding groups from the values of dipolar term P .

The reduction of P values from the free ion value (0.036 cm^{-1}) might be attributed to the strong covalent bonding³⁷⁰. The lower P and α^2 T values for [AMPDTC] Mn complex suggest the presence of strong in-plane π bonding which in agreement with higher ligand field. The shape of ESR lines, ESR data together with the electronic spectral data suggest square planar geometry for copper complex³⁷¹.

Table.4. Spin Hamiltonian and orbital reduction parameters of Mn complex in DMF solution

Parameters	Mn (AMPDTC) ₂
g_{\parallel}	2.2373
g_{\perp}	2.1699
g_{ave}	2.2290
G	2.5369
A_{\parallel}^*	0.0113
A_{\perp}^*	0.0016
A_{ave}^*	0.0062
$d-d$	25600
K_{\parallel}	0.6241
K_{\perp}	0.8052
P^*	0.0301
α^2	0.3990

Thermal Analysis of [AMPDTC] Mn and [AMPDTC] Fe complex:

TG techniques were employed to follow the thermal behaviour of complexes. According to the results obtained, the complexes are not volatile and their decomposition occurs in different steps. The typical Thermogram of [AMPDTC] Mn complex is shown in the Fig.8. Thermogravimetric studies on the complexes confirmed their proposed molecular formulae. The [AMPDTC] Mn complex is thermally stable upto 171°C . The thermogram of the complex shows a First stage of decomposition around 196.35°C to 257.26°C , which indicates the presence of lattice water and this decomposition corresponds to endothermic dehydration of the complex^{9,10} and gives anhydrous complex. The second decomposition stage with two (or) three endothermic peaks is known as stable intermediate formed around 229.55°C and they under goes decomposition resulting in the loss of ligand moiety at 292.44°C and 497.56°C . Exothermic decomposition takes place to give the corresponding Manganese sulphide as the final decomposition product at a high temperature i.e above 801.30°C . The decomposition behaviour of the complexes is observed in nitrogen atmosphere. All the experimental mass loss and total mass loss percentage values found were presented in the table.5.

TG techniques were employed to follow the thermal behaviour of complexes. According to the results obtained, the complexes are not volatile and their decomposition occurs in different steps. Thermogravimetric studies on the complexes confirmed their proposed molecular formulae. The typical Thermogram of [AMPDTC] Fe complex is shown in the Fig.9. The [AMPDTC] Fe complex is thermally stable upto 179.78°C . The thermogram of the complex shows an First stage of decomposition around 102.45°C to 168.54°C , which indicates the presence of lattice water and this decomposition corresponds to endothermic dehydration of the complex and gives anhydrous complex. The second decomposition stage with two (or) three endothermic peaks is known as stable intermediate formed around 249.73°C and they under goes decomposition resulting in the loss of ligand moiety at 362.44°C and 590.16°C . Exothermic decomposition takes place to give the corresponding Iron sulphide as the final decomposition product at a high temperature i.e above 930°C . The decomposition behaviour of the complex is observed in nitrogen atmosphere. All the experimental mass loss and total mass loss percentage values found were presented in the table.5.

Table.5. Thermal analytical data of the Ligand and their metal complexes:

Complex-X=H ₂ O	Molecular weight in gms	Weight of the complex taken in mgs	Temperature Range during weight loss in °C	% of Fraction of weight	Probable assignment
[Mn.L ₂ .X ₂] L= C ₇ H ₇ N ₂ S ₂	438.938	8.1910	90-180 230-590 Above 590	5.1580 78.8033 9.5913	Loss of 2H ₂ O molecule. Loss of two L molecules. Remaining residue Corresponds to MnO.
[Fe.L ₂ .X ₂] L=C ₇ H ₇ N ₂ S ₂	439.847	12.1630	70-210 430-590 Above 590	5.5135 84.2341 17.1439	Loss of 2H ₂ O molecule. Loss of two L molecules. Remaining residue Corresponds to FeO.



Conductivity Measurements of Metal complexes:

The molar conductance of complexes in DMF ($\sim 2 \times 10^{-3}$ M) was determined at $27 \pm 2^\circ\text{C}$ using Systronic 303 direct reading conductivity bridge. The dithiocarmate metal complexes of Manganese (II) and Iron (III) are prepared from the 2-Amino-6-methyl pyridine and Carbon disulphide. It was observed that these complexes are soluble in dimethylformamide (DMF). Therefore, these metal chelates are dissolved in DMF to perform conductivity measurements.

A known amount of solid complex is transferred into 25ml standard flask and dissolved in dimethylformamide (DMF). The contents are made up to the mark with DMF. The complex solution is transferred into a clean and dry 100ml beaker and the conductivity values are measured. The specific and molar conductance values are calculated using the equations (1) and (2) respectively. If the Molar conductance value (k) is more than $10 \text{ Ohm}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$ the metal complexes are said to be electrolytic in nature. If the k value is less than $10 \text{ Ohm}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$ the metal complexes are said to be non-electrolytic in nature. The conductivity measurements are used for the determination of electronic nature of the metal complexes.

The conductance values of all the metal complexes are given in Table.6. the molar conductance values for all the newly synthesized complexes are in the range $2.53 - 2.99 \text{ Ohm}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$ which indicates the non-electrolytic nature.

Table:6. Conductance data for M [AMPDTC] complexes
(with cell constant 1.00)

Metal Complex	Conductance (Ohm's)	Specific conductance ($\text{Ohm}^{-1} \cdot \text{cm}^{-1}$)	Molar conductance ($\text{Ohm}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$)
[AMPDTC] ₂ Mn	0.035×10^{-3}	0.035×10^{-3}	35
[AMPDTC] ₂ Fe	0.025×10^{-3}	0.025×10^{-3}	25

Magnetic susceptibility measurements of Metal complex:

The effective magnetic moment values for all the complexes are represented in the Table.7. The magnetic moments of the present (AMPDTC)₂ Mn complex is 3.42 B.M. This value suggests the formation of low-spin complex, and electronic spectral data suggest the square planar geometry for the Manganese complex. The (AMPDTC)₂ Fe complex shows magnetic moment 3.70 B.M. and this value is less than the spin-only value, showing reduced paramagnetism, which suggest the formation of low-spin complex having octahedral geometry. The study of magnetic measurements revealed that the complexes are showing reduced paramagnetism suggesting that the the ligand is strong and the complexes formed were low-spin, inner orbital complexes.

Table.7. Magnetic moments of Metal chelate complexes

Metal Complex	Magnetic moment (B.M)
(AMPDTC) ₂ Mn	3.42
(AMPDTC) ₂ Fe	3.70

Powder X-ray Diffraction studies of AMPDTC-Mn and AMPDTC-Fe complex:

The diffractogram record (16 diffractions) reflects Fig.10., between 2θ (2 θ) values. Where θ is Brages angle. All the main peaks are indicated and calculated values of Miller indices (h k l) along with observed d-specocofoed and 2θ are specified in the Table.8. All the Peaks have been indexed and 2θ values compared in graph. Comparison values reveals that there is good agreement between values of 2θ and d-values^{11,12,13}. The powder X-ray diffraction data showed identical features [84] with very poor crystallinity. The patterns are qualitative and dispersive in intensity for Molybdenum complex. The XRD patterns are used to explain qualitatively the degree of crystallinity. The diffractogram record (13 diffractions) reflects Fig.11. between 2θ (2 θ) values. Where θ -is Brages angle. All the main peaks are indicated and calculated values of Miller indices (h k l) along with observed d-specocofoed and 2θ are specified in the Table.9. All the Peaks have been indexed and 2θ values compared in graph. Comparison values reveals that there is good agreement between values of 2θ and d-values. The powder X-ray diffraction data showed identical features [84] with very poor crystallinity. The patterns are qualitative and dispersive in intensity for Vanadium complex. The XRD patterns are used to explain qualitatively the degree of crystallinity.

Table.8. X-ray Diffraction data of AMPDTC-Mn Complex:

S.No.	2θ expt	2θ calc	d expt	d calc	h k l
1	11.64455	11.64454	7.59322	7.59345	2 1 1
2	13.88366	13.88366	6.37324	6.37332	4 1 1
3	17.64759	17.64760	5.02150	5.02154	5 2 1
4	19.07534	19.07534	4.64875	4.64878	5 4 2
5	20.04740	20.04736	4.42549	4.42549	6 4 2

6	22.64731	22.64728	3.92298	3.92299	8 7 1
7	24.63296	24.63294	3.61106	3.61108	8 6 1
8	26.72232	26.7223	3.33327	3.33331	9 8 3
9	28.71865	28.71864	3.10594	3.10728	10 7 2
10	30.13617	30.13622	2.96299	2.96301	10 9 1
11	31.16592	31.16594	2.86740	2.86743	11 9 0
12	38.90770	38.90774	2.31282	2.31284	12 6 1
13	39.95965	39.95962	2.25433	2.25435	12 8 3
14	41.62096	41.62086	2.16811	2.16812	14 9 2
15	45.87737	45.87724	1.97637	1.97636	14 11 2
16	47.83538	47.83530	1.89994	1.89995	16 10 1

Table:9. X-ray Diffraction data of AMPDTC-Fe Complex:

S.No.	2 θ expt	2 θ calc	d expt	d calc	h k l
1	5.74963	5.749636	15.35833	15.35952	2 1 0
2	10.12735	10.12724	8.72712	8.727239	3 2 1
3	12.43091	12.43004	7.11460	7.115093	4 3 1
4	15.57899	15.57968	5.68330	5.68346	6 3 2
5	18.01738	18.01688	4.91927	4.91940	7 5 2
6	19.19132	19.19084	4.62092	4.62103	8 6 0
7	21.25106	21.24996	4.17747	4.17767	9 6 5
8	24.90087	24.90028	3.57281	3.57289	9 7 2
9	26.28889	26.28890	3.38723	3.38726	10 8 5
10	28.19587	28.19468	3.16233	3.16245	11 8 2
11	34.47616	34.47580	2.59929	2.59931	12 9 2
12	36.60534	36.60452	2.45283	2.45288	14 2 0
13	50.37448	50.37348	1.80996	1.81005	14 11 2

Antibacterial activity**Method Employed**

To prove the antibacterial activity of the ligand and metal complexes on bacteria paper disc diffusion procedure was employed.

Medium

Nutrient agar medium was employed for the testing. Peptone (5g) was dissolved in a liter of distilled water. Beef extract (5g) was added to the peptone solution and agar (15g) was mixed. The contents were mixed thoroughly and the pH was adjusted to 7.4-7.6. The solution was sterilized in the autoclave for 10-15 minutes at 15 lbs. per sq. inch pressure, to prove the same.

Testing Equipment

Petri plates of same size, hot air oven, Autoclave, sterilized pipettes and filter paper. The present investigation is an attempt to find out the antibacterial activity of ligand and their metal complexes^{14,15} against *Escherichia coli*, *Klebsiella* and *Bacillus subtilis* in the range 50-150 $\mu\text{m/ml}$. Choosing serial paper disc diffusion method. The Antibacterial activity results were given in the Table.6.(1). the results of the biological activity of the metal complexes indicated the following facts.

A comparative study of the ligand and their complexes indicates that most of the metal chelates exhibited higher antibacterial activity than that of the free ligand. The increase in the antibacterial activity of metal chelates was explained on the basis of overtones concept and chelation theory.

Table.10. Antibacterial activities of ligands and their transition metal complexes (Zone formation in mm)

Compound	E.Coli	KLEBSIELLA	BACILLUS
AMPDTC	6	8	7
(AMPDTC) ₂ Mn	10	11	13
(AMPDTC) ₂ Fe	15	13	12

Conclusion:

Finally basing on the above information it can be concluded that 2-amino 6-methyl pyridine dithiocarbamate ligand act as a very good complexing agent towards many transition metal ions. By using above spectral studies it is concluded that they behave as bidentates during complexation. All the metal complexes carry no charge and are thermally stable. As such no single technique is independent of predicting final

structures of the complexes, the entire information available from all the studies is clubbed together and tentative structures of the complexes under investigation have been formulated as follows Fig.12.

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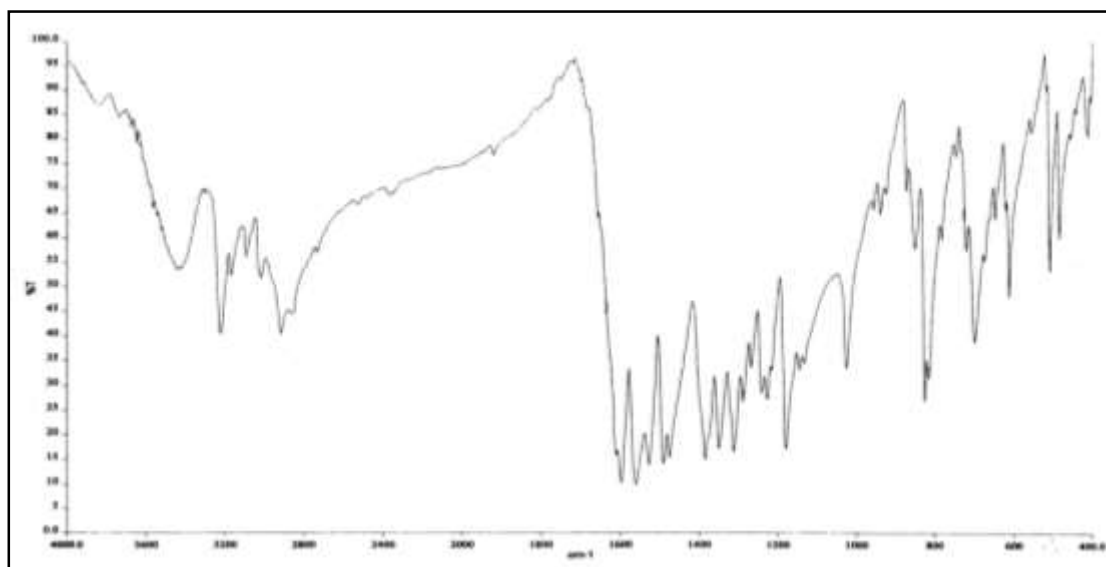


Fig. 1. IR SPECTRUM OF AMPDTC Ligand

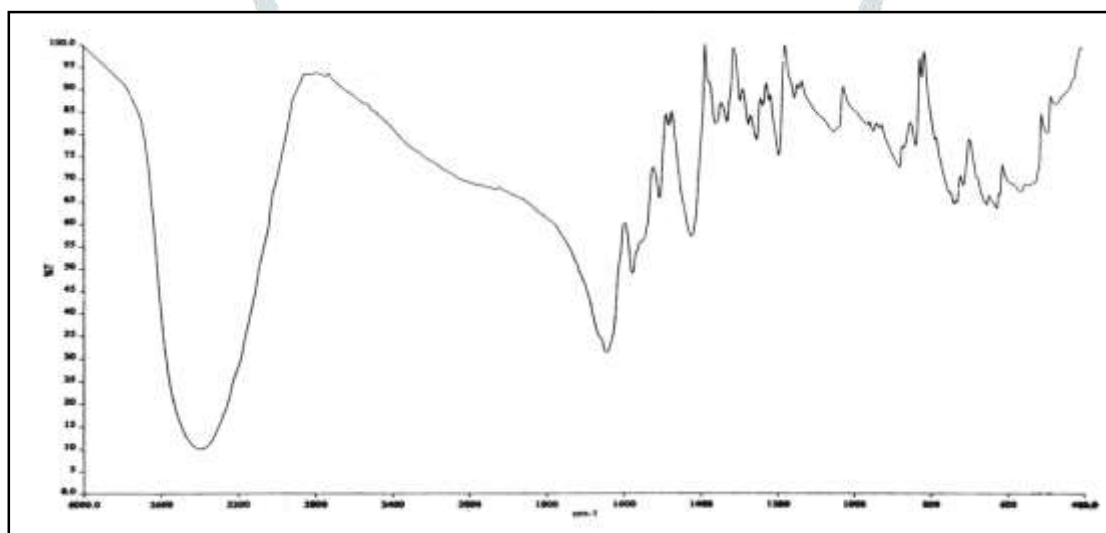
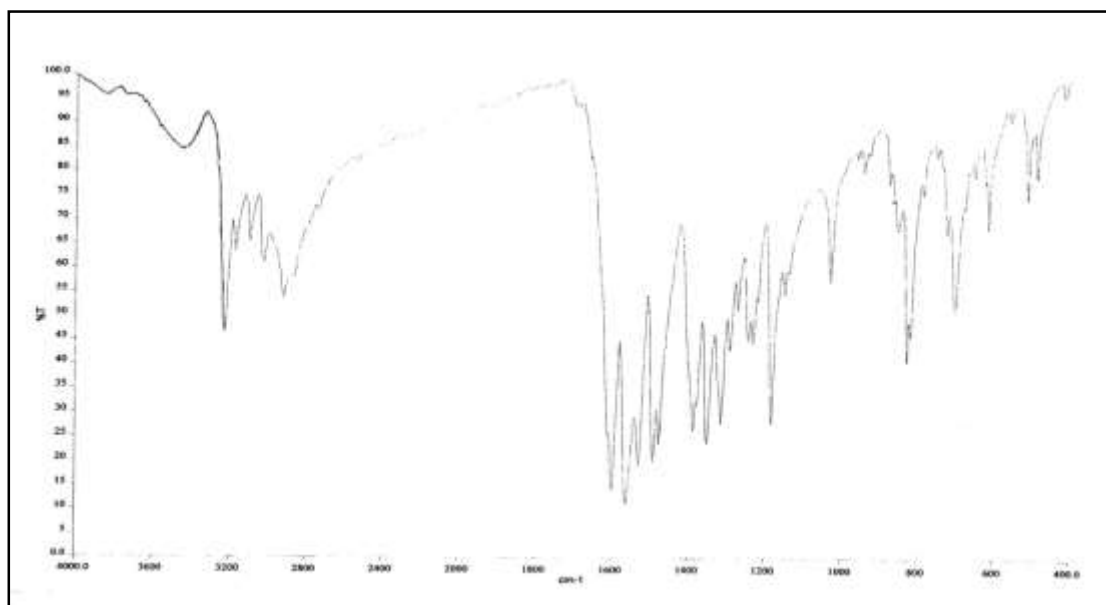
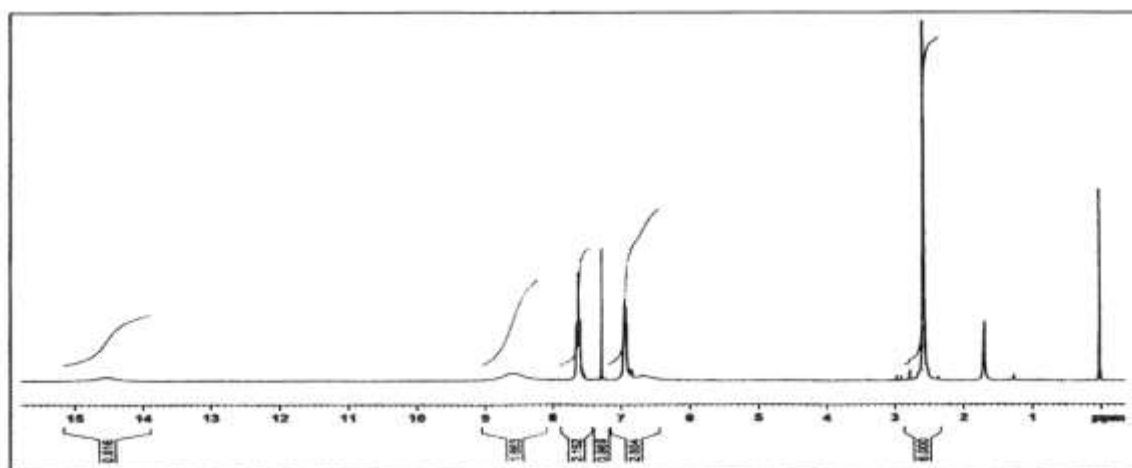
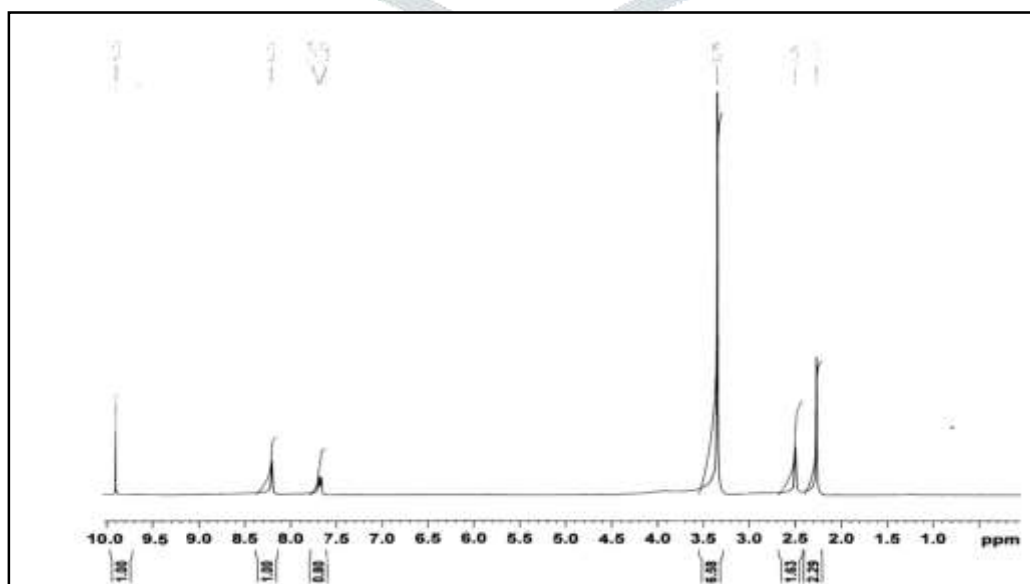


Fig. 2. .IR SPECTRUM OF AMPDTC –Mn Complex

**Fig. 3. IR SPECTRUM OF AMPDTC –Fe Complex****Fig.4. NMR SPECTRUM OF AMPDTC Ligand****Fig.5. NMR Spectrum of AMPDTC-Mn Complex**

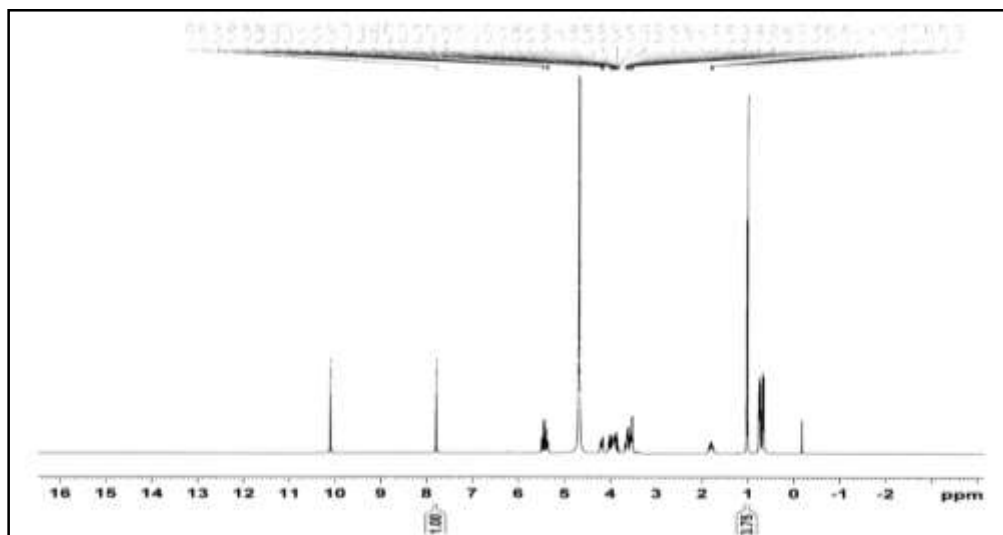


Fig. 6. NMR Spectrum of AMPDTC-Fe Complex

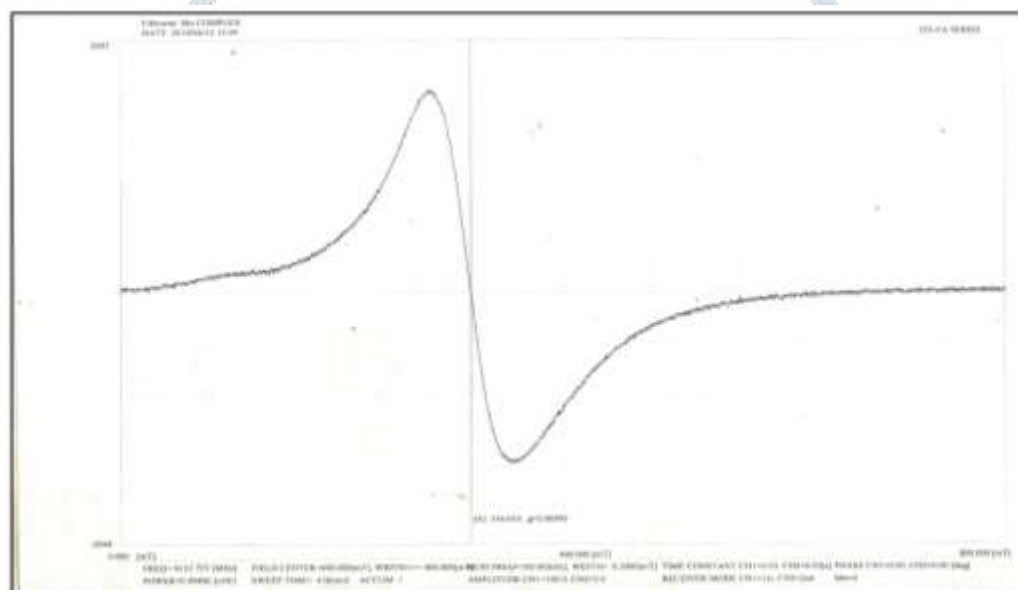


Fig. 7. ESR Spectrum of AMPDTC-Fe Complex

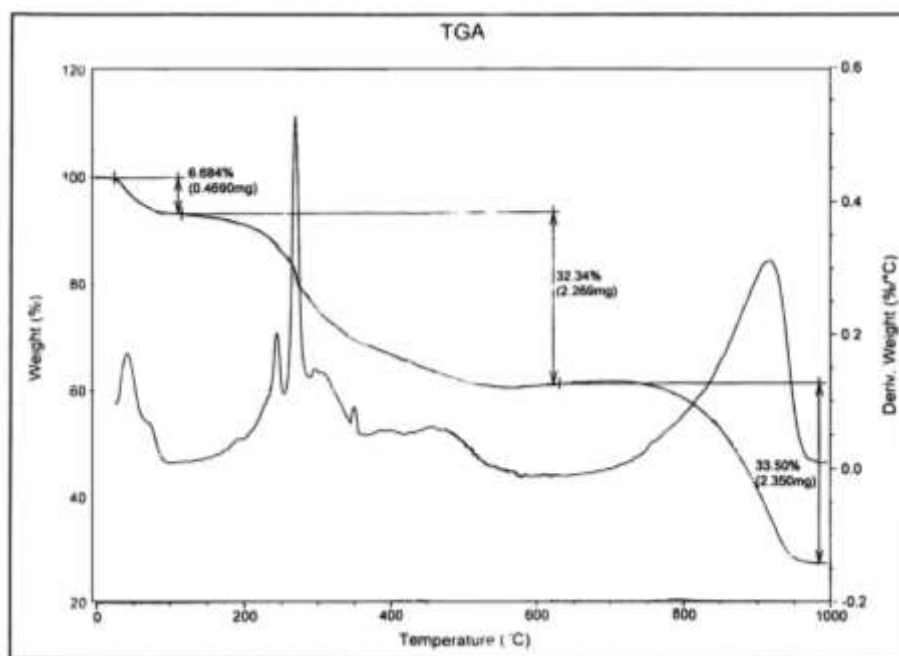


Fig.8.TGA&DTA SPECTRUM OF AMPDTC-Mn Complex

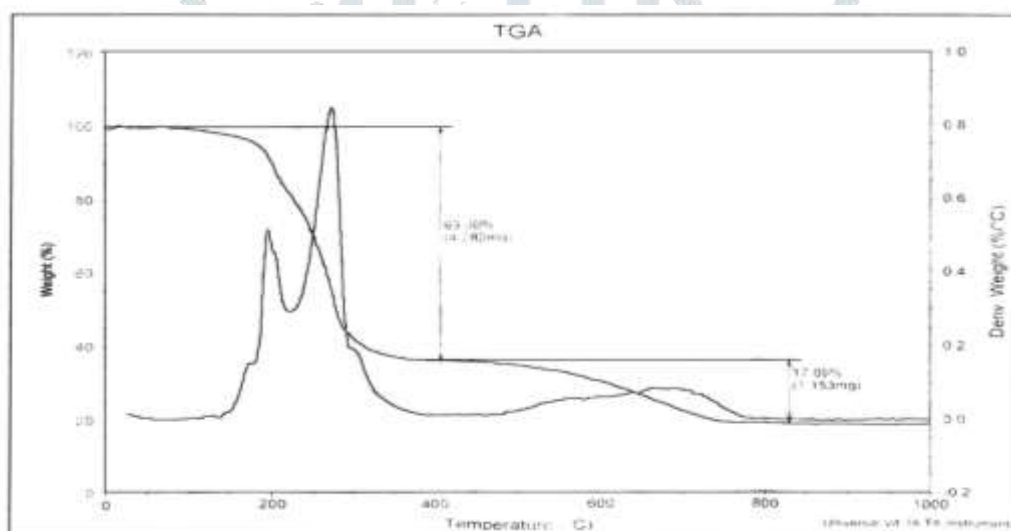


Fig.9. TGA&DTA SPECTRUM OF AMPDTC-Fe Complex

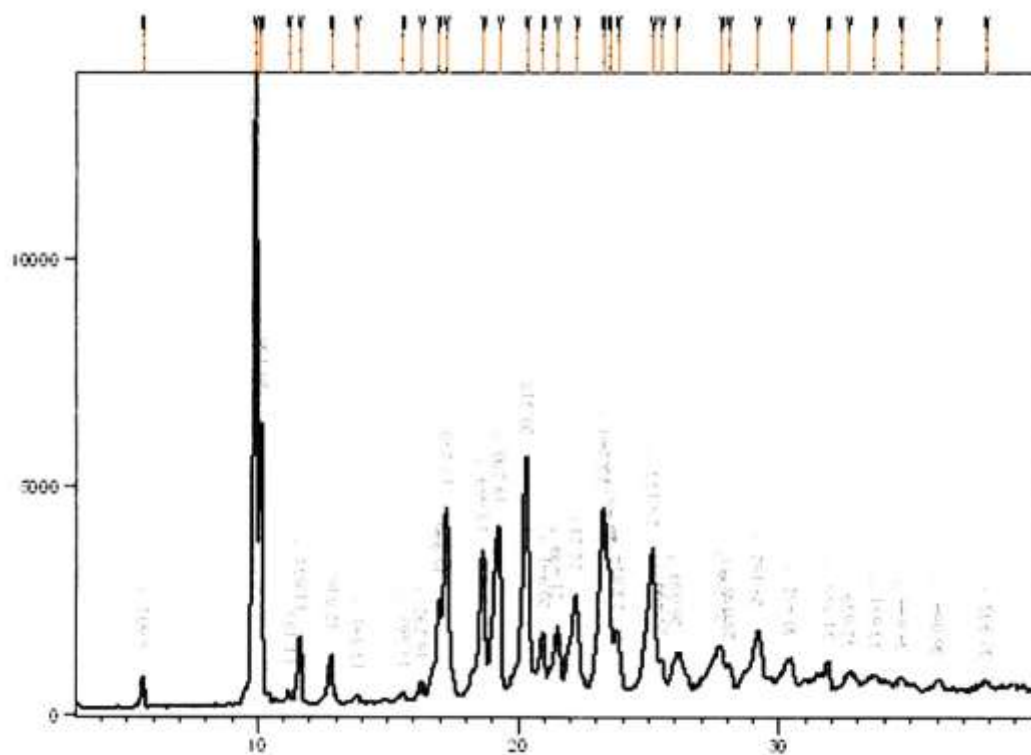


Fig.10.PXRD SRECRUM OF AMPDTC-Mn complex

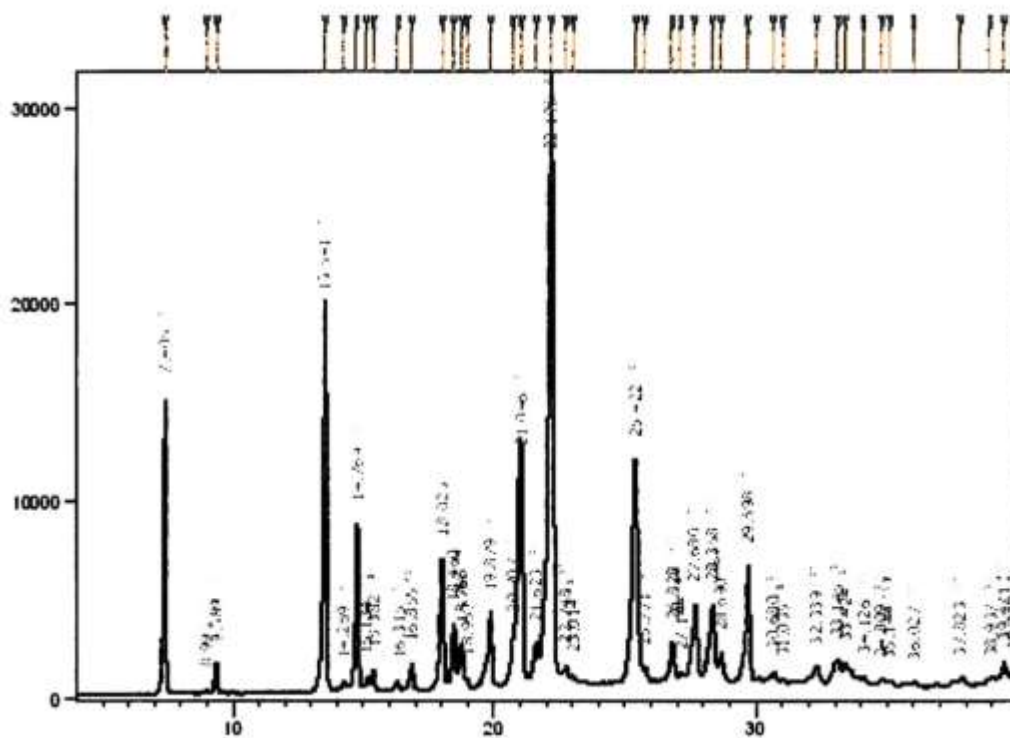


Fig.11. PXRD SRECRUM OF AMPDTC-Fe complex.

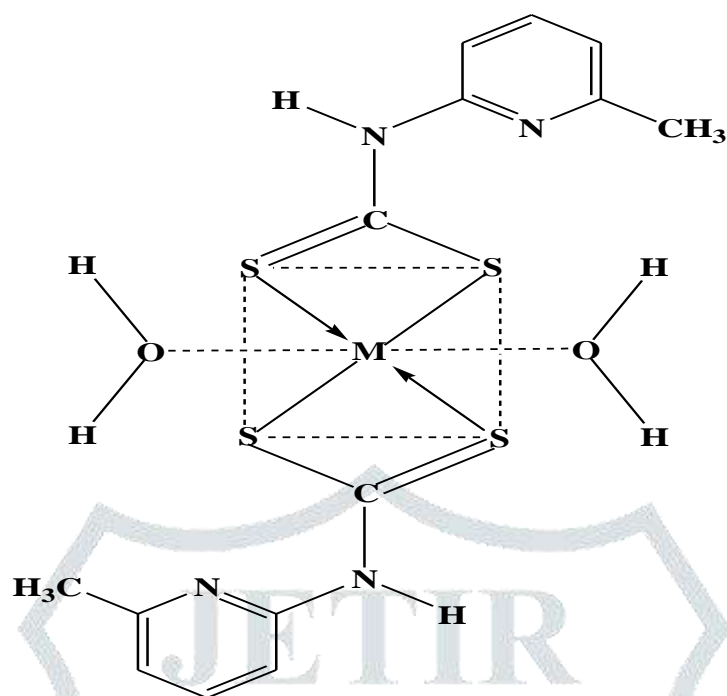


Fig. 12. Structure of metal complexes $(AMPDTC)_2Mn$ & $(AMPDTC)_2Fe$