Synthesis and Characterization of Mn(II),Co(II) and Ni(II) Complexes of Schiff Base Ligand derived from 4-amino antipyrine

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Abstract

In this study, transition metal complexes of Mn(II),Co(II) and Ni(II) were synthesized from the aromatic Schiff base ligand derived from 4-aminoantipyrine and p-dimethyl amino benzaldehyde to give the following ligand 4-(4-dimethylamino benzylidene amino)-1,5-dimethyl-2-phenyl-pyrazol-3-one .The structural features were derived from their elemental analyses, melting point, infrared and UV-visible spectroscopy. The FT.IR spectral data suggest the involvement of oxygen of the ring C= O and nitrogen of the azomethine CH = N group in coordination to the central metal ion.

Key words: Schiff base ligand ,4-aminoantipyrine, metal complexes, p-Dimethyl amino benzaldehyde .

1.Introduction

Schiff bases (or Hugo Schiff)[1] is a functional group that contains a -C=N These are condensed products of Carbonyl compounds and primary amines[2] have a wide variety of applications in many fields such as, coordination chemistry[3,4], analytical chemistry [5], pigments and dyes[6], and polymer industries[7], in vitamins and enzymes[8] for model biomolecules. Schiff bases are well known to have antifungal, antitumor and herbicidal activities[9-12]. in addition to their important rols in catalysis and organic synthesis[13]. Some research groups found that the Schiff base metal complexes derived from 4-aminoantipyrine can specially cleave the DNA[14-16] and have a variety of application in analytical and biological areas[17,18].

Schiff bases of 4-amino antipyrine and its complexes have a variety of application in biological, clinical, and pharmacological areas[19].Properties of 4-amino antipyrine to coordinate with metal is varied by condensing it with aldehydes, ketones, thio semicarbazides and carbazidesetc., Metal complexes of 4-amino antipyrine and biological behavior involving the amino group of 4-aminoantipyrine has been studied exhaustively, when compared to the work carried out on the chemistry of transition metal complexes and biological behavior involving the amino group of 4-amino antipyrine[20-24].The aim of the present study was to synthesize and characterize Mn(II) ,Co (II)and Ni (II) metal complexes with newly synthesized Schiff base ligand derived from 4-aminoantipyrine and , *p*-dimethyl aminobenzaldehyde.

2.Experimental

Materials and physical measurements

All chemicals used were of highest purity (BDH and Fluka) and used without further purification .Micro analysis of carbon, hydrogen and nitrogen were obtained using elemental analyzer,.Absorption spectra were recorded by Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Magnetic Susceptibilities were measured as powder samples using Faraday method, a balance Magnetic MSB-MKI was employed for this purpose .Electrical conductivity measured by digital conductivity meter Alpha – 800 with the prepared complexes concentration of 10^{-3}M in ethanol at room temperature. pH measurements were carried out using (pH– meter), 720 , WTW 82362.

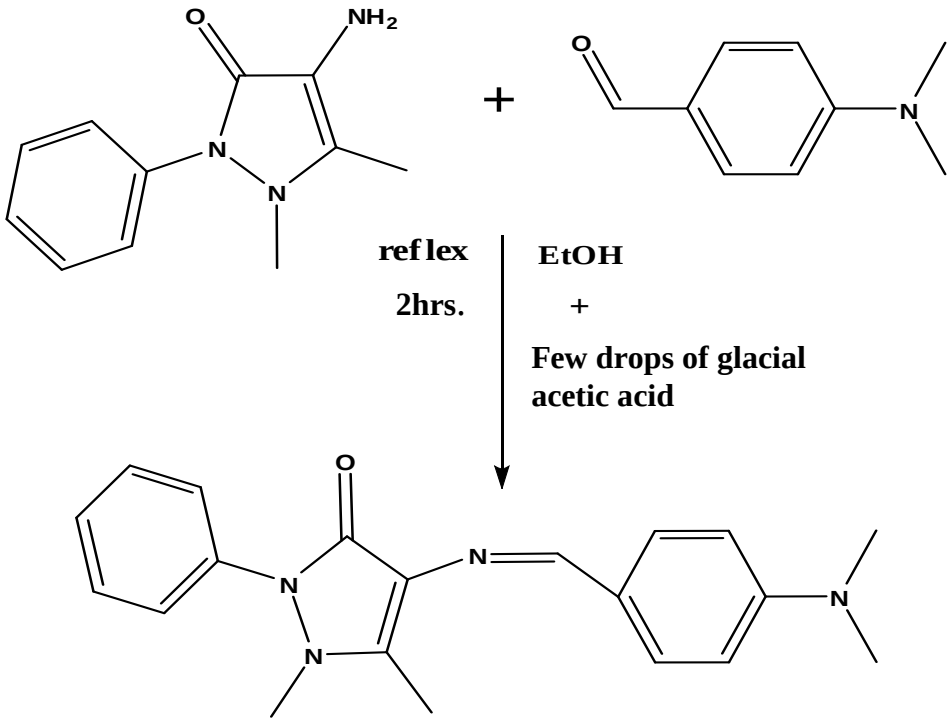
Preparation of Schiff base (DBAB)[25]

The Schiff base from 4-dimethylaminobenzaldehyde and 4-aminoantipyrine was prepared by adding an ethanolic solution (20 mL) of 4-dimethylaminobenzaldehyde (1.49 g ; 0.01 mol) to an ethanolic solution of 4-aminoantipyrine (2.03 g ; 0.01 mol)(scheme 1**)**.

The mixture was stirred for two hours, and the resulting mixture was evaporated under vacuum to remove the solvent. The obtained product was collected by filtration ,washed several times with methanol and recrystallized from hot ethanol and then dried under vacuum .The melting point of the yellow crystals found to be 256 ^{o}C.

Preparation of Schiff base complexes

The mixtures of the Schiff base under investigation (0.01 mmol; 3.34 g) in 30 ml ethanol and metal salts [10mmol, $MnCl_2.4H_2O$ (1.2g), $CoCl_2.6H_2O$ (2.37g), $NiCl_2.6H_2O$ (2.37g), in the same amount of the same solvent were refluxed for three hours. The complexes were collected by filtration and then washed several times with hot ethanol until the mother liquors become colorless. The resulted products were dried in air and stored in a desiccator over anhydrous $CaCl_2$ under vacuum .They decomposed above 359 ^{o}C



Scheme 1: **General route for the synthesis of Schiff base ligand (DBAB)**

3.Results and Discussion

The analytical data for the ligands and their complexes together with some physical properties are summarized in Table 1.All complexes show the conductivity measurement values ranging between (12 – 19) $S.cm^2.mol^{-1}$ in ethanol solution at room temperature ,these values indicating nonionic structure of these complexes.

Table 1 Physical characterization, analytical, molar conductance and magnetic susceptibility data of the Schiff bases and their complexes

No.	Molecular formula	Found (Calc.) (%)			Formula weight	Λm $S.cm^2.mol^{-1}$	Yield (%)	μ_{eff} BM
		C	H	N				
1	$C_{20}H_{22}N_4O$	71.44 (71.83)	6.55 (6.63)	16.88 (16.75)	334.41	-----	----	----
2	$[Mn(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	48.21 (48.40)	5.17 (5.28)	11.37 (11.29)	491	19	72	5.65
3	$[Co(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	47.91 (48.02)	5.14 (5.24)	11.32 (11.20)	495.3	16	77	5.06
4	$[Ni(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	47.96 (48.04)	5.09 (5.24)	11.29 (11.20)	495	12	81	3.12

Effect of pH

To evaluate optimal pH values on the absorbance for the metal complexes solution were studied in the 50% (V/V) ethanolic solution in the range of (5 – 10) as shown in Fig.1. The Schiff base ligand formed a very stable complexes with metal ions Mn(II), Co(II) and Ni(II) wide pH range.

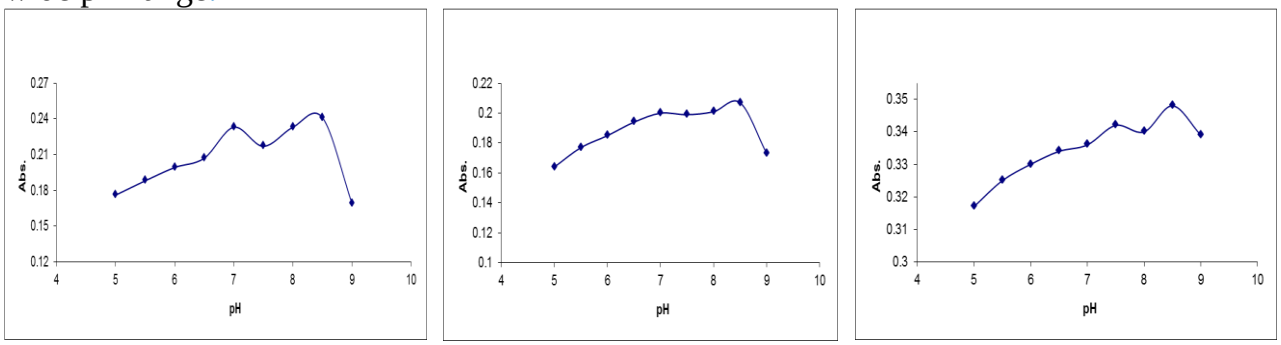


Figure 1: The effect of pH on the absorbance of Mn(II),Co(II) and Ni(II) complexes

Absorption spectra

The absorption spectra of Schiff base ligand [26]and its complexes were studied. The wavelength for the maximum absorption (λ_{max}) of the ligand was found at 359nm. The spectra of metal complexes were recorded within wavelength range (435– 349) nm. The absorption maxima(λ_{max}) of the each complexes is shown in Table.2.Two absorption bands appeared for the Schiff base ligand. The band at 238 nm referred to the $\pi \rightarrow \pi^*$ transitions of antipyrine ring while the band at 359nm assigned to $n \rightarrow \pi^*$.The UV-Vis spectra of the complexes(Mn(II),Co(II) and Ni(II)) showed absorption peaks at (239, 351nm), (241, 349nm) and (351,435nm) which were assign to ligand field and charge transfer transition respectively The spectrum of the complexes shows relative change in the bands position compared to that of the ligand ,as showed in figures(**2-5**).

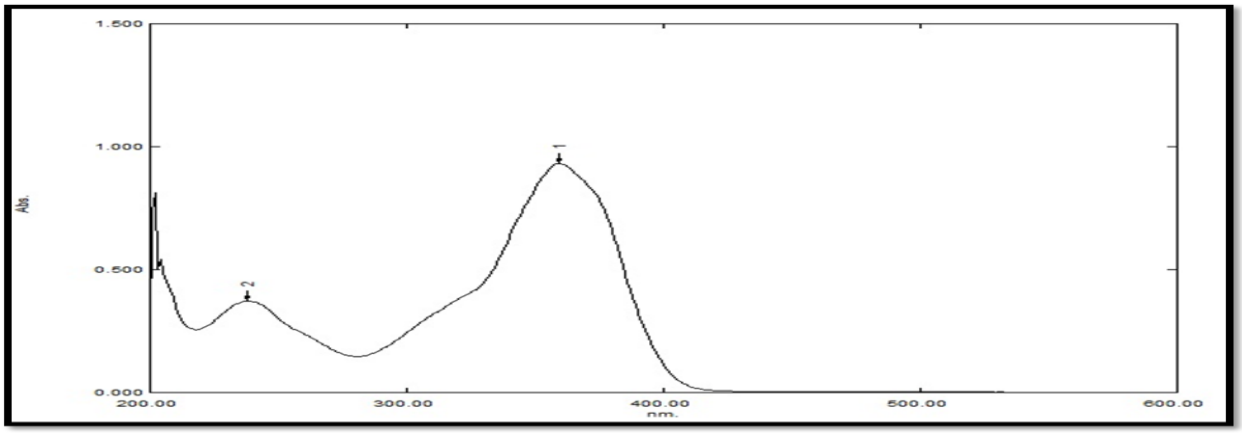


Figure (2): Absorbance spectrum of Schiff base ligand (DBAB)

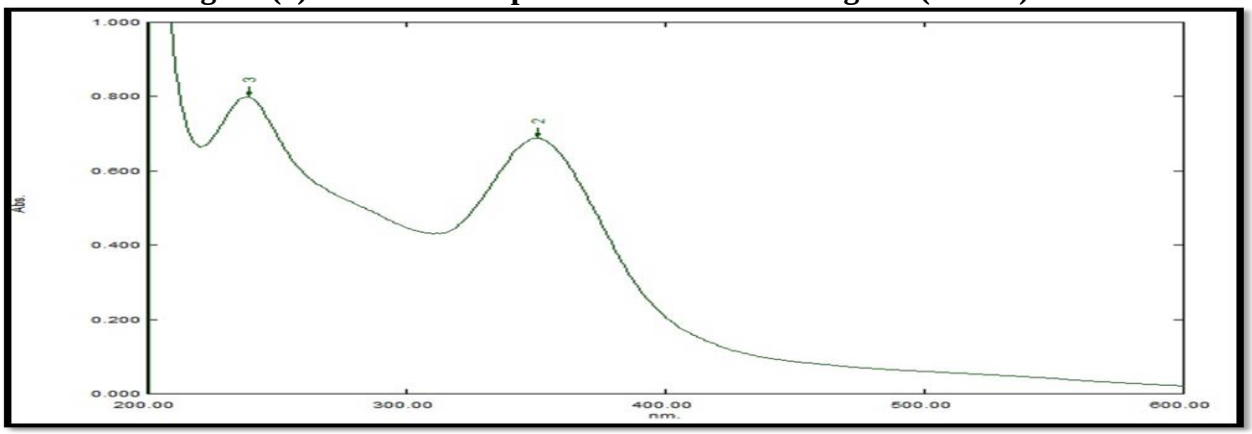


Figure 3.Electronic spectrum of Mn (II) Complex

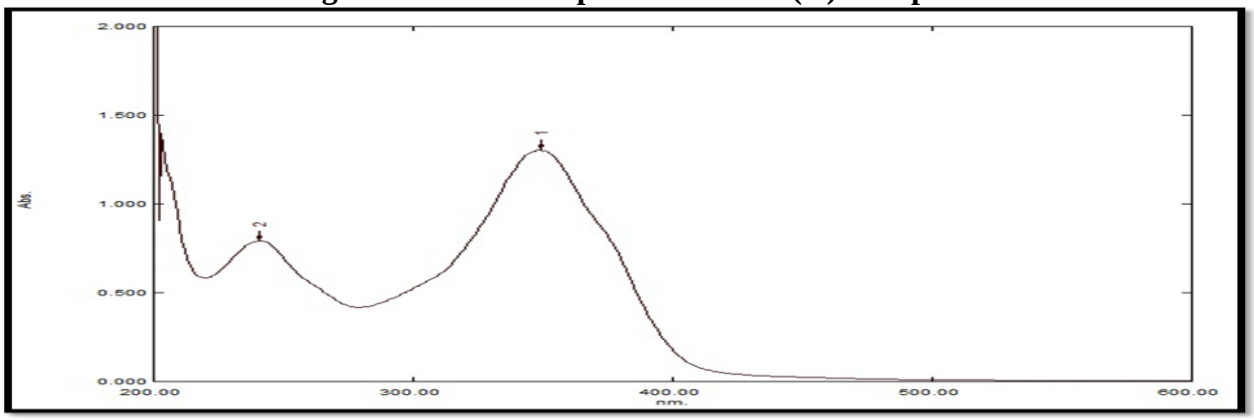


Figure 4.Electronic spectrum of Co (II) Complex

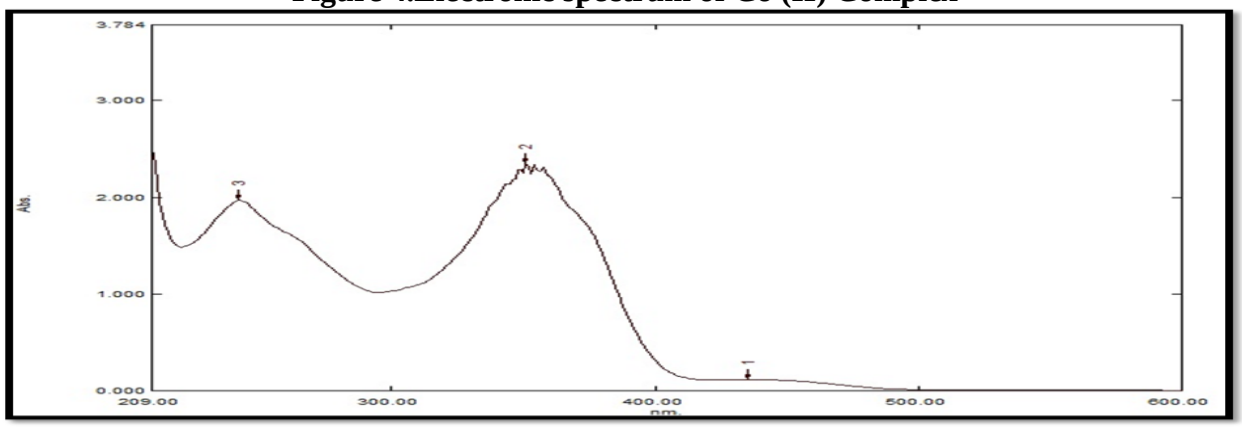


Figure 5.Electronic spectrum of Ni (II) Complex

Infrared spectral studies of the ligand and its complexes

The data of the IR spectra of Schiff base and its complexes were compared with the IR spectra of the free ligand in order to determine the involvement of coordination sites in chelation and to detect the changes that might have taken place. The obtained data are summarized in Table 2 with some assignments of the important characteristic bands

Table 2: Some IR frequencies in (cm–1) of the ligand and its metal complexes

No.	Compounds	*ν* (O-H) water	ν(C=N)	ν (C=O)	ν(M-N)	ν(M-O)
1	$C_{20}H_{22}N_4O$	----	1610	1647	----	----
2	$[Mn(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	3447	1614	1654	601	501
3	$[Co(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	3440	1612	1649	592	422
4	$[Ni(C_{20}H_{22}N_4O)(Cl)_2(H_2O)_2]$	3382	1608	1646	590	445

The infrared spectra of these complexes **(Figures 6,7,8 and 9)** exhibit a broad band in the range of (3245-3500 cm^{-1}) due to the presence of water molecules. The absorption bands in the range of (1608-1614) cm^{-1} are assigned to the existence of ν(HC=N-) group of the azomethine . The changing of this group to higher frequency indicates the affected of this group by complexation[27]**.** The other coordination site, which can take a part in coordination is the (C=O) group, the strong evidence of sharing of this group can be seen from the position of the band at (1647 cm^{-1}) in the spectrum of free ligand. The shifting of this band to higher frequency in the spectra of the complexes suggest the participation of (C=O) group in chelation**.** New bands in the range of (590-601) cm^{-1} and (422-501) cm^{-1} which are not present in the free Schiff base are due to ν(M-N) and ν(M–O) vibrations and the appearance of these vibrations support the involvement of nitrogen and oxygen atoms of azomethine and carbonyl groups of the free Schiff base in complexation with the metal ions under investigation

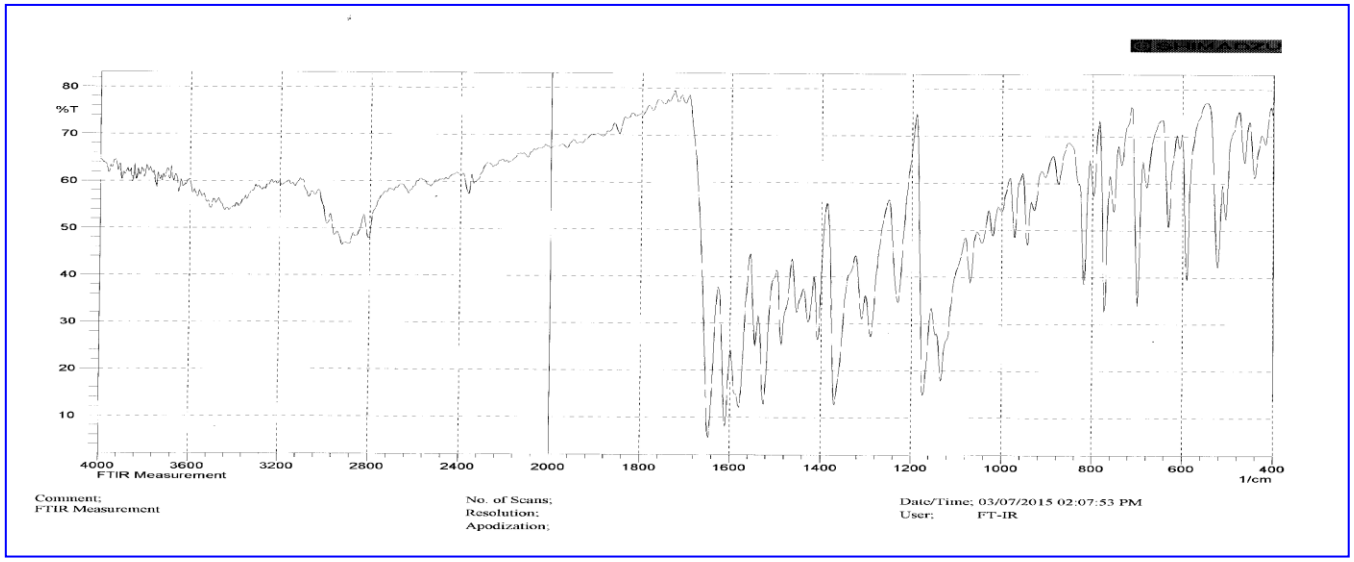


Figure (6): FT-IR spectrum of Schiff base ligand (DBAB)

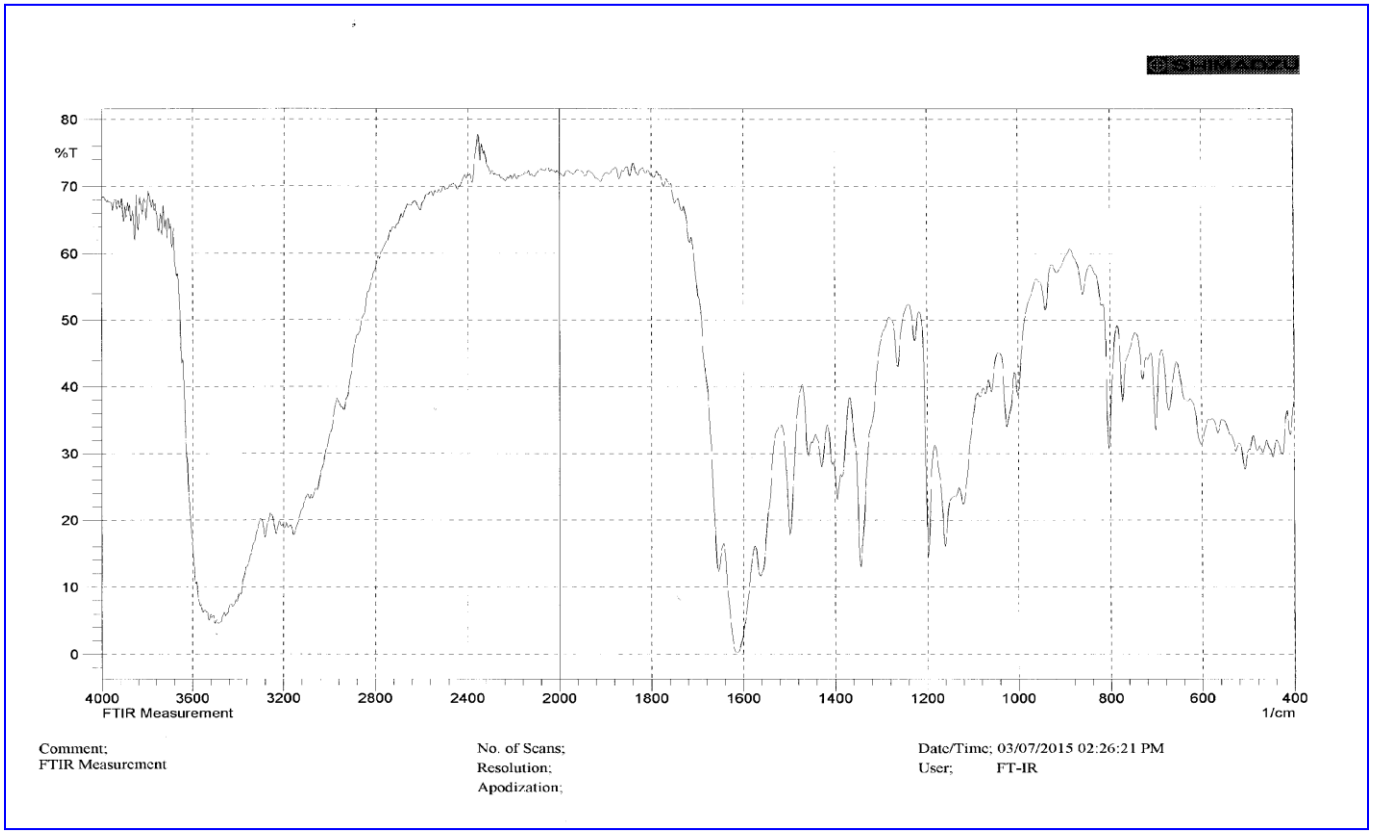


Figure (7): FT-IR spectrum of Mn(II)-complex

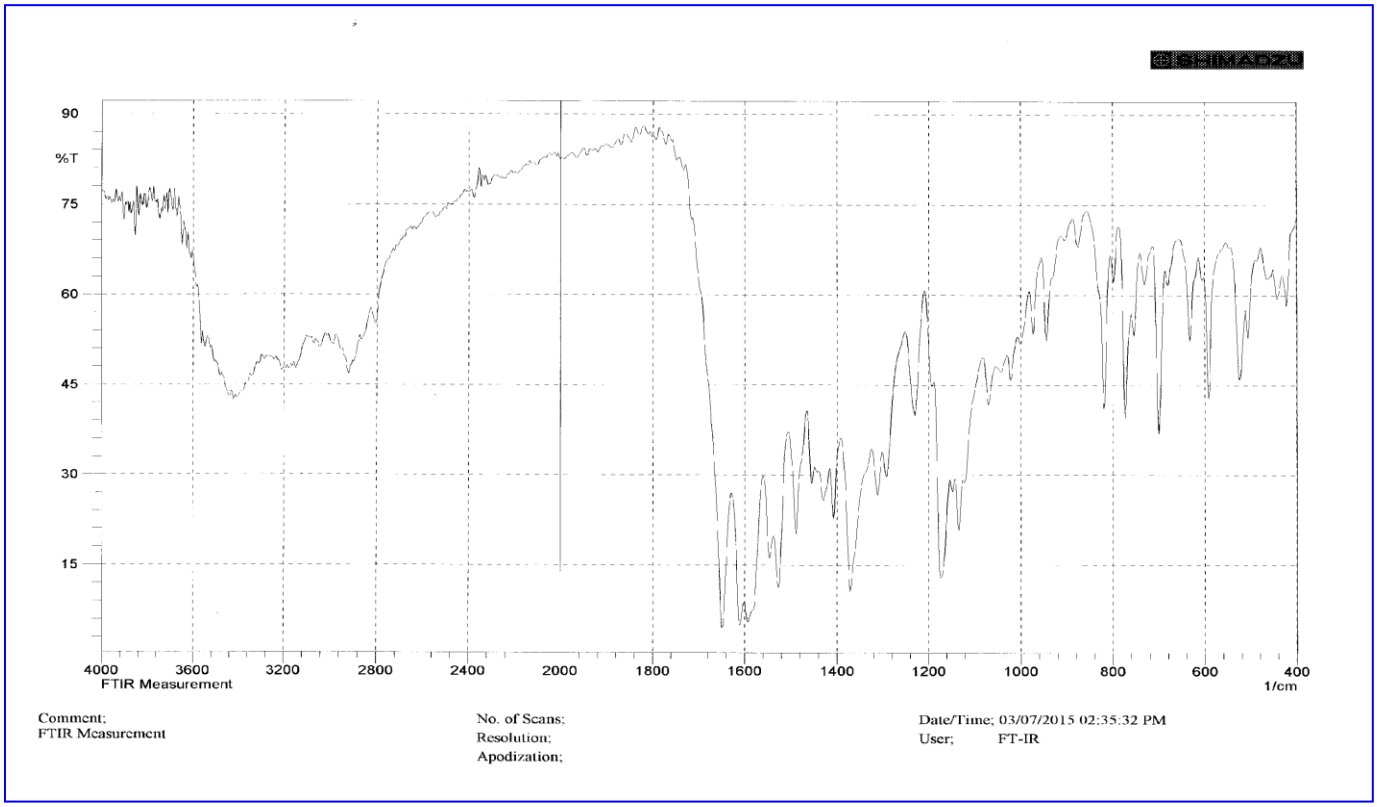


Figure (8): FT-IR spectrum of Co(II)- complex

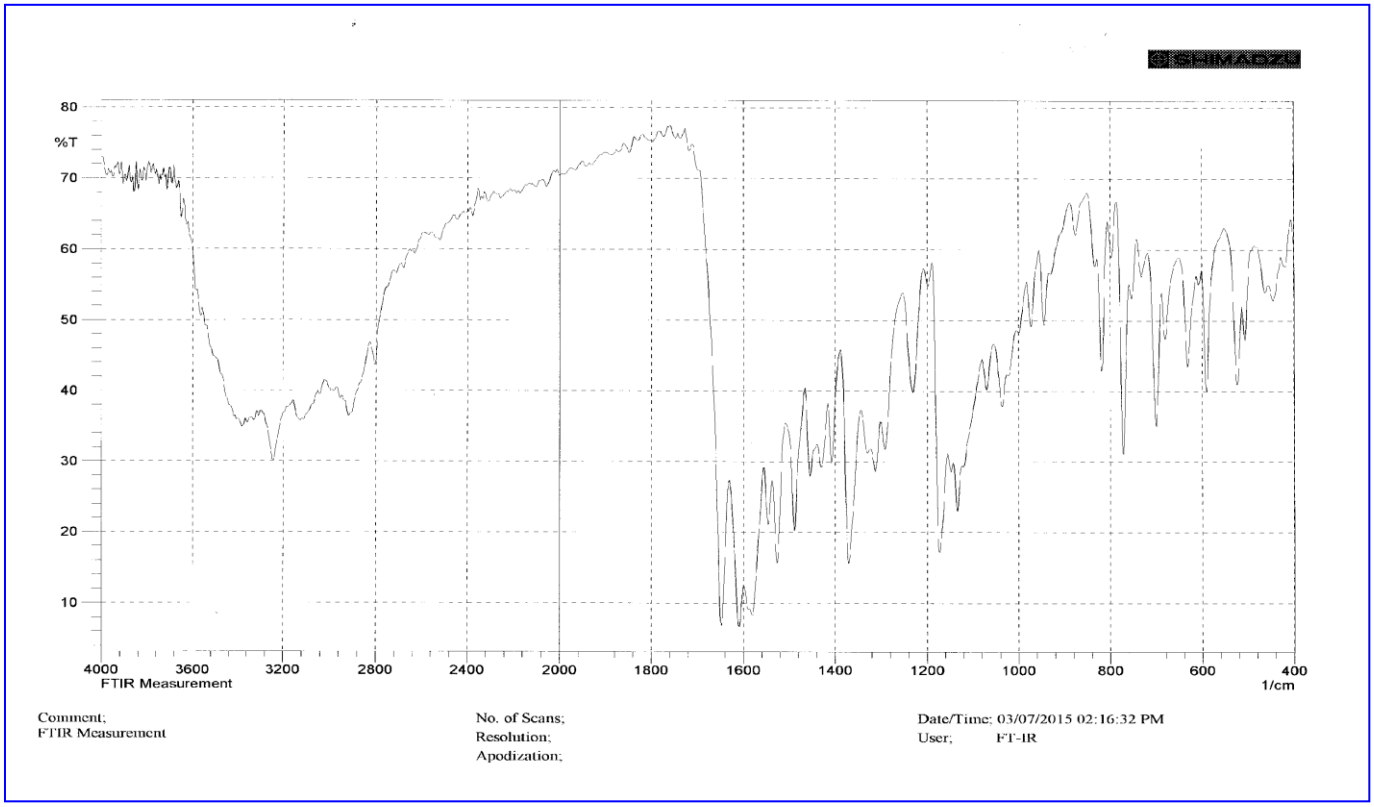


Figure (9): FT-IR spectrum of Ni(II) - complex

4.CONCLUSION

This paper report the preparation and identification of Schiff base ligand and its complexes with Mn(II),Co (II) and Ni (II) metal ions. The isolated products were characterization by available techniques. All the proposed geometry of the complexes are octahedral. According to these results the structural formulas of these complexes may be proposed in Figure 10.

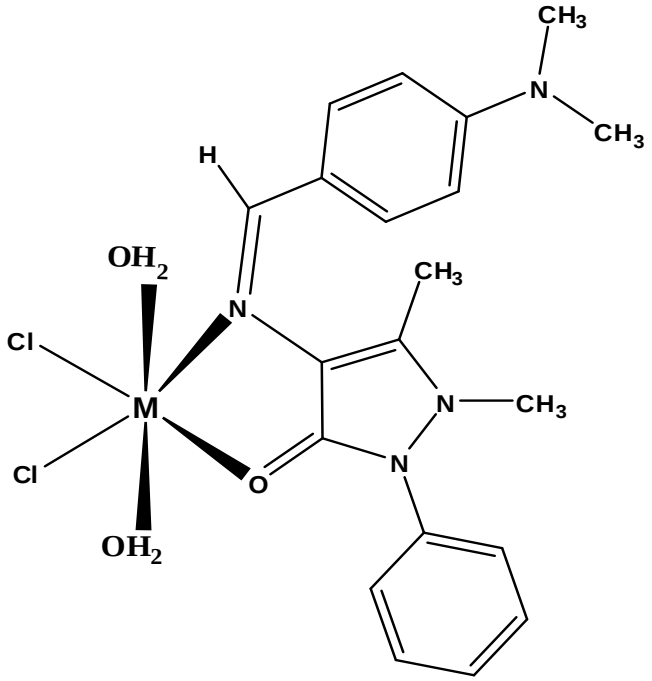


Figure 10:The proposed structural formula of Mn(II) Co(II) and Ni(II) with Schiff base ligand

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الخلاصة :-

في هذا البحث ،تم تحضير بعض معقدات العناصر الأنتقالية لأيونات المنغنيز **(II)** والكوبلت **(II)** والنيكل **(II)** مع ليكاند قاعدة شف **(DBAB)** المشتق من المركب 4- أمينو أنتي بايرين والمركب بارا ثنائي مثيل امينو بنزالديهايد . شخصت المركبات المحضرة بواسطة التحليل الدقيق للعناصر والحساسية المغناطيسية عند درجة حرارة الغرفة ، والتوصيلية المولارية وأطياف الأشعة تحت الحمراء والأطياف الإلكترونية . أثبتت بيانات الأطياف الإلكترونية والحساسية المغناطيسية أن الشكل الهندسي المقترح للمعقدات المحضرة هو الشكل ثماني السطوح وبينت أطياف الأشعة تحت الحمراء إرتباط أوكسجين مجموعة الكاربونيل ونتروجين مجموعة الآزوميثين بآيون الفلز المركزي.