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RESEARCH ARTICLE

Preparation and Characterization of some transition metal complexes of bis Schiff Base Ligand

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Abstract

In the study, transition metal complexes of Mn(II),Co(II) and Ni(II) were synthesized from the aromatic Schiff base ligand derived from 4-aminoantipyrine , p-dimethyl amino benzaldehyde , p-amino benzaldehyde to give the following ligand 4-(4-(4-dimethyl aminobenzylideneamino)benzylideneamino)-1,5-dimethyl-2-phenyl-pyrazol-3-one. The ligand and its metal complexes (II) are characterized on the basis of elemental analyses, magnetic moment measurements, molar conductance , melting point, infrared and UV-visible spectroscopy. On the basis of the studies the coordination sites were proven to be through oxygen of the ring C=O and nitrogen of the azomethine CH=N group. From the observations, the octahedral geometric structure for the synthesized complexes were suggested.

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, thiosemicarbazides and carbazides etc., 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 bis Schiff base ligand derived from 4-aminoantipyrine, p-amino benzaldehyde and , *p*-dimethyl amino benzaldehyde.

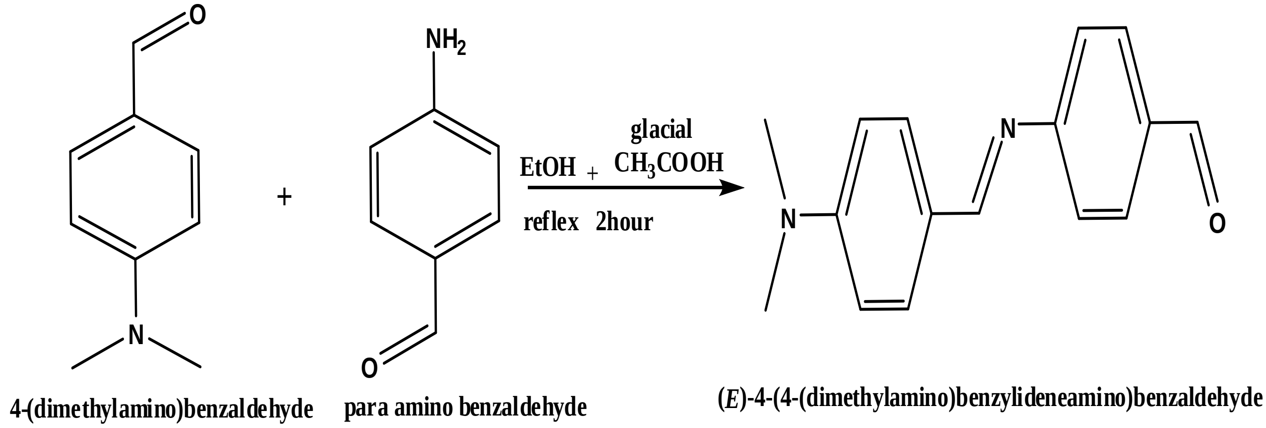
2. Experimental

2.1. Measurements

All chemicals used were of highest purity (BDH and Fluka) 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, 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

2.2. Preparation of Schiff base(I):

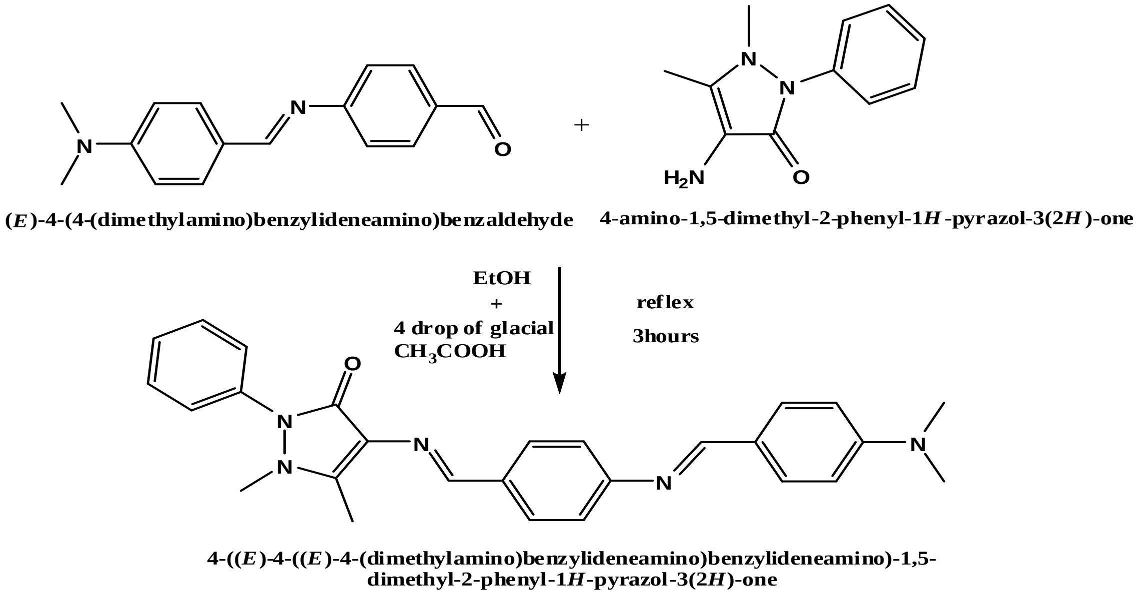
20mL absolute ethanol solution of p-amino benzaldehyde (1.06g /0.01mol) was added to 20mL absolute ethanol solution of p-dimethyl amino benzaldehyde (1.34 g/ 0.01 mol) in the presence of 5 drops of acetic acid as a catalyst. The mixture was refluxed for 2 h. The resultant solution was cooled to room temperature. The yellow solid of 1-(4-(4-hydroxy-3-methoxybenzylideneamino)phenyl)ethanone was formed which was filtered and recrystallized in absolute ethanol (scheme 1). Yield; 85%: m.p: 201°C.



Scheme 1: **The Preparation of Schiff base(I)**

2.3. Preparation of Schiff base ligand (II)[(25)]

An ethanolic solution of 4-aminoantipyrine (2.03 g, 0.01mol, 20 ml) was taken in a burette and added drop wise to the ethanolic solution of 4-(4-dimethylamino) benzalidene amino) benzaldehyde (2.5 g, 0.01 mol, 20 ml),Add 6 drops of glacial acetic acid with constant stirring for 4 hours. The dark yellow precipitate compound (II) was the obtained by filtration and recrystallized from hot ethanol, and dried over anhydrous $CaCl_2$. (scheme 2) m.p-295°C



Scheme 2: ***Preparation of Schiff base ligand (II)***

2.4.Preparation of Schiff base complexes

The mixtures of the bis Schiff base under investigation (0.01 mole; 3.34 g) in 30 ml ethanol and metal salts [0.01mole, $MnCl_2.4H_2O$ (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. The resulted products were dried in air and stored in a desiccator over anhydrous $CaCl_2$ under vacuum .They decomposed above 354 ^{o}C

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	$C_{16}H_{16}N_2O$	76.11 (76.16)	6.36 (6.39)	11.12 (11.10)	252.31	-----	85	----
2	$C_{27}H_{27}N_5O$	74.02 (74.12)	6.18 (6.22)	16.13 (16.01)	424.21	-----	76	----
3	$[Mn(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$	53.98 (54.10)	5.09 (5.21)	11.73 (11.68)	599.41	18	72	5.65
4	$[Co(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$	53.65 (53.74)	5.13 (5.18)	11.64 (11.61)	603.41	13	77	4.91
5	$[Ni(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$	53.67 (53.76)	5.09 (5.18)	11.72 (11.61)	603.17	15	81	3.12

3.1.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(п), Co(п) and Ni(п) wide pH range.

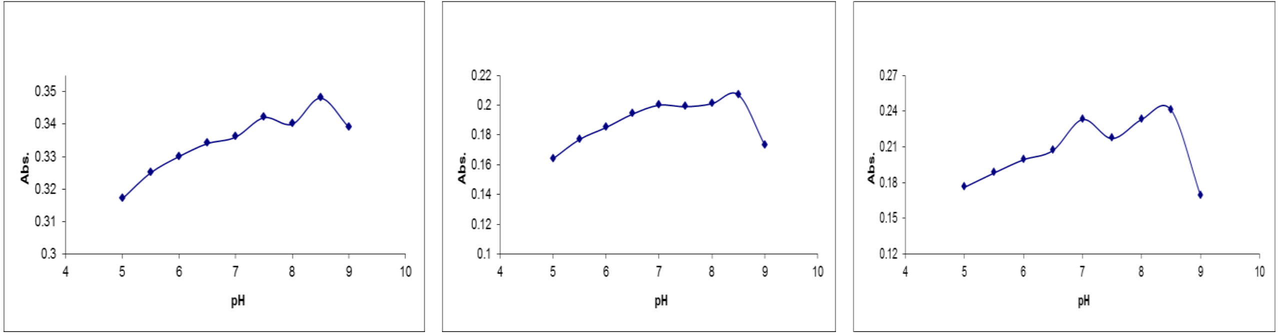


Figure 1: The effect of pH on the absorbance of Mn(II),Co(II) and Ni(II) complexes

3.2.Absorption spectra

The absorption spectra of Schiff base(II) ligand and its complexes were studied$^{(26)}$. The wavelength for the maximum absorption (λ_{max}) of the Schiff base (I) was found at 341nm while the (λ_{max}) of Schiff base (II) ligand was found at 360nm. The spectra of metal complexes were recorded within wavelength range (241– 360) nm. The absorption maxima (λ_{max}) of the each complexes. Two absorption bands appeared for the Schiff base(I) at 243 nm which referred to the ($\pi\rightarrow\pi^*$) transitions of benzene ring while the band at 341nm assigned to ($n\rightarrow\pi^*$).The UV-visible spectra of the Schiff base (II) ligand showed two bands at 242nm and 360nm assigned to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions within the molecule .The UV-Vis spectra of the complexes Mn(II),Co(II) and Ni(II) showed absorption peaks at (242, 346nm), (241, 340nm) and

(242,268,339nm) 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(**2-6**).

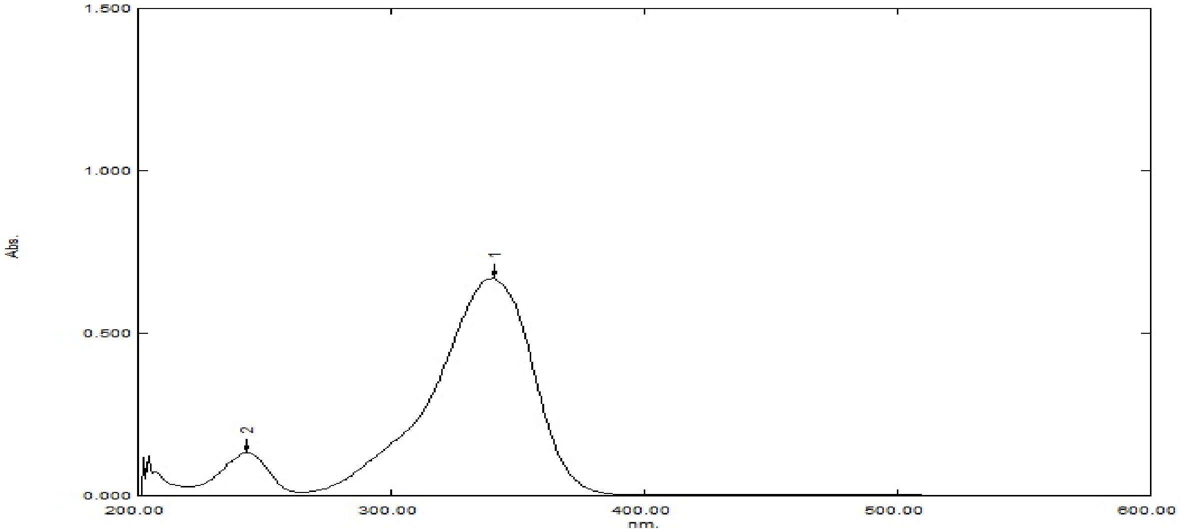


Figure 2: Absorbance spectrum of Sciff base ligand

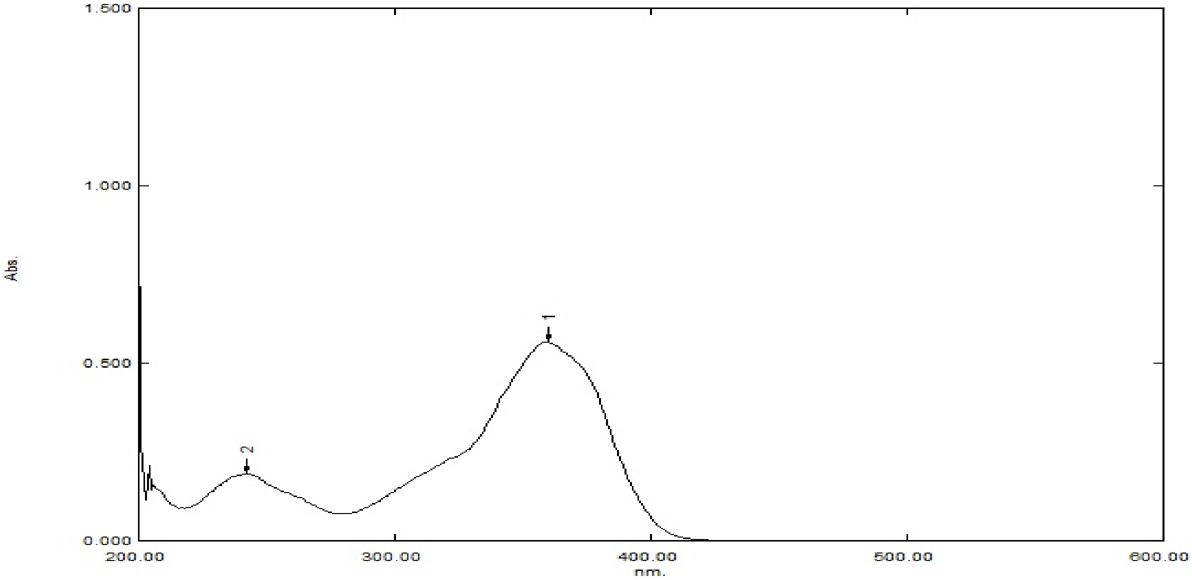


Figure 3: Absorbance spectrum of bis Schiff base ligand

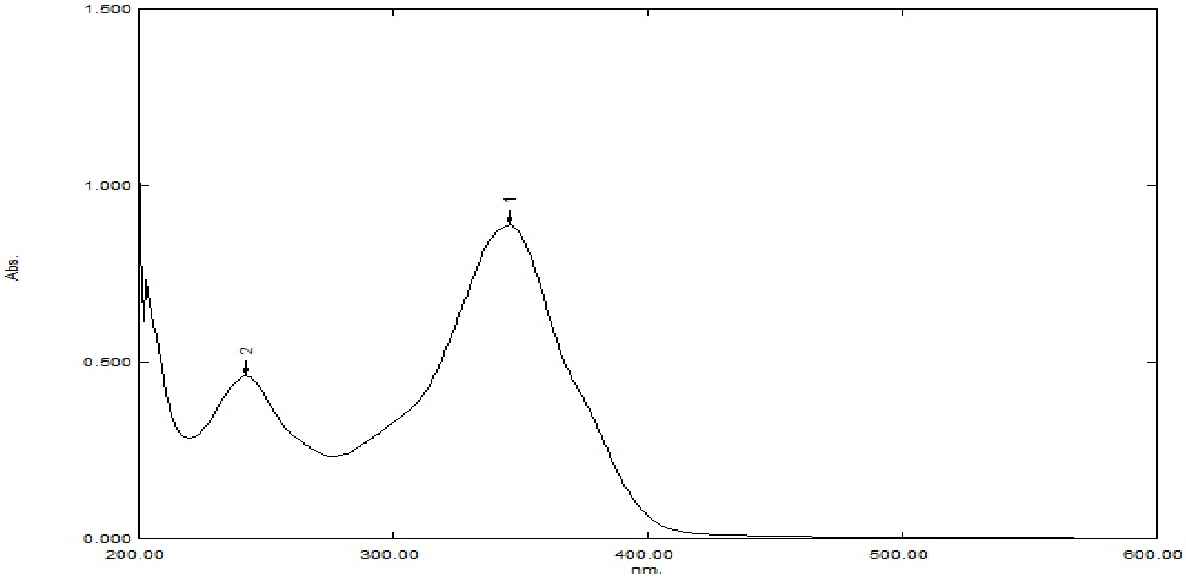


Figure 4.Electronic spectrum of Mn (II) Complex

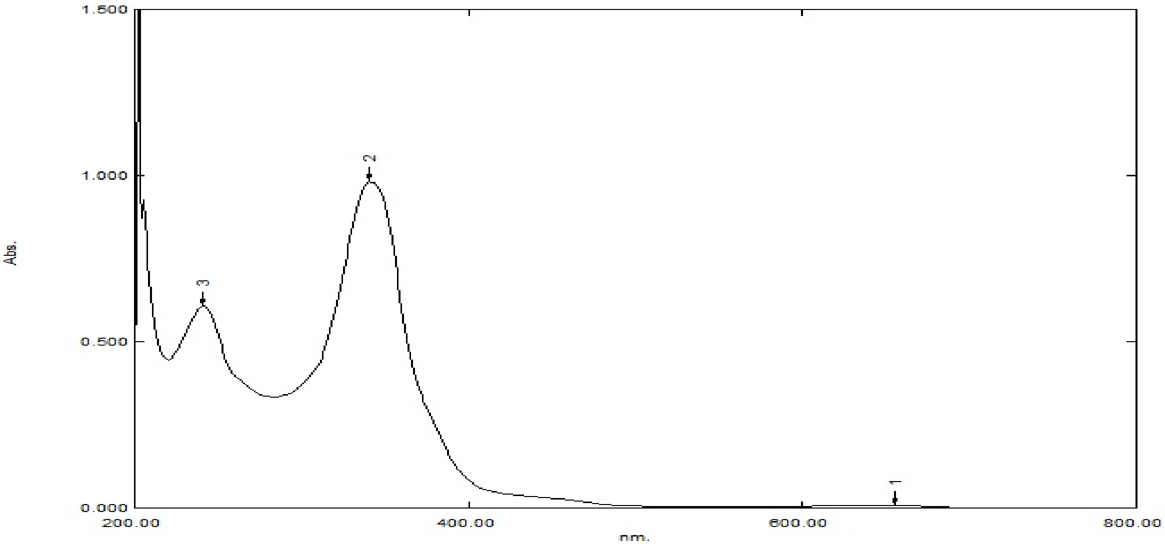


Figure 5.Electronic spectrum of Co (II) Complex

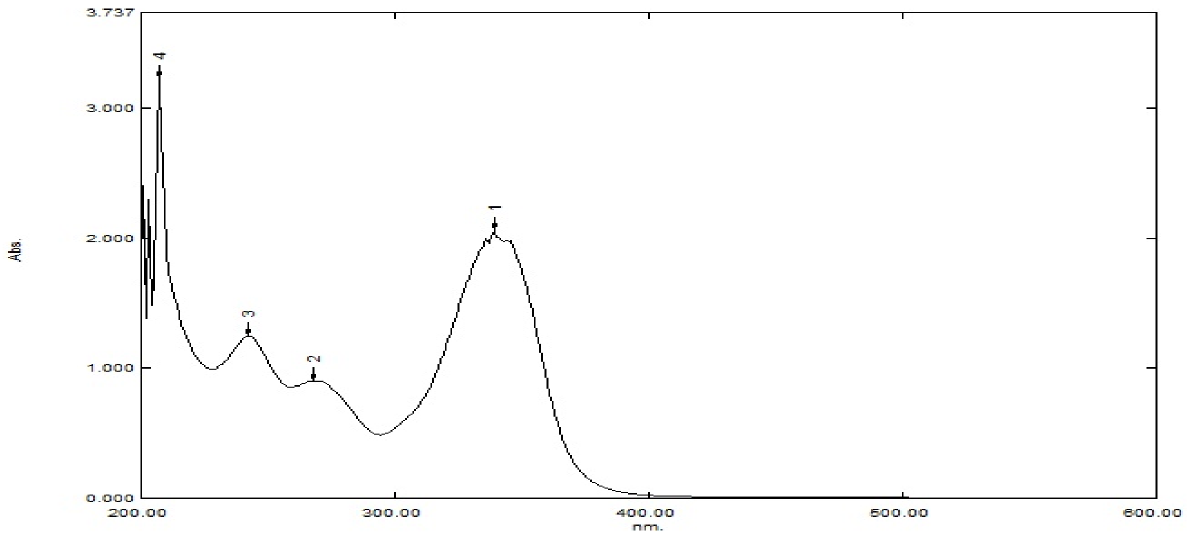


Figure 6.Electronic spectrum of Ni (II) Complex

3.3.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	**$C_{16}H_{16}N_2O$**	----	1596	1658	----	----
2	**$C_{27}H_{27}N_5O$**	----	1610	1647	----	----
3	**$[Mn(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$**	3447	1611	1647.4	501	601
4	**$[Co(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$**	3440	1612	1649	422	592
5	**$[Ni(C_{27}H_{27}N_5O)(Cl)_2(H_2O)_2]$**	3382	1608	1646	445	590

The infrared spectra of these complexes **(figures 7-11)** 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.

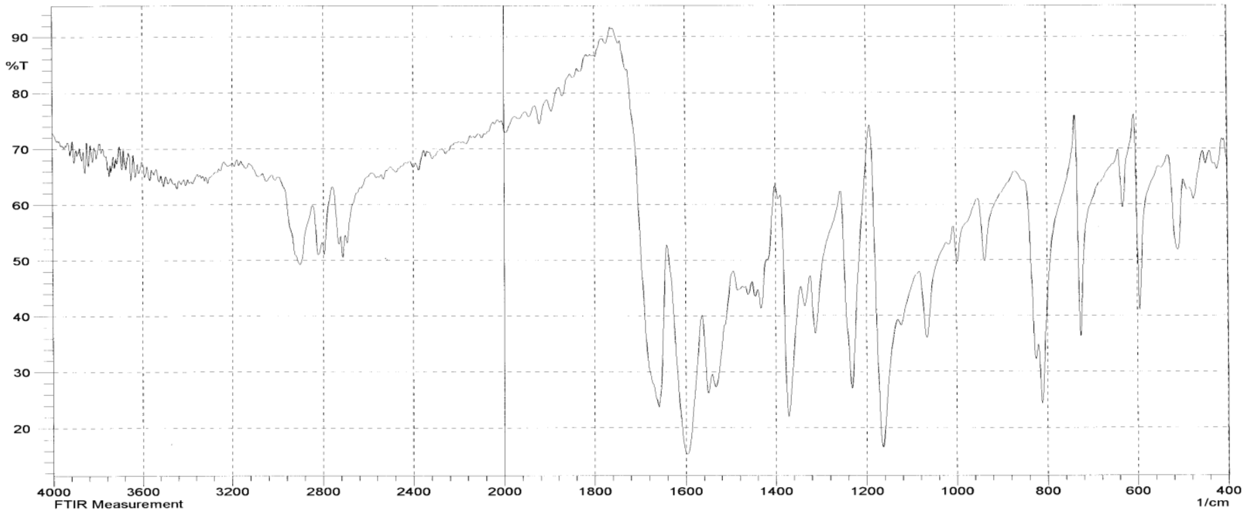


Figure 7: FT-IR spectrum of Schiff base (I)

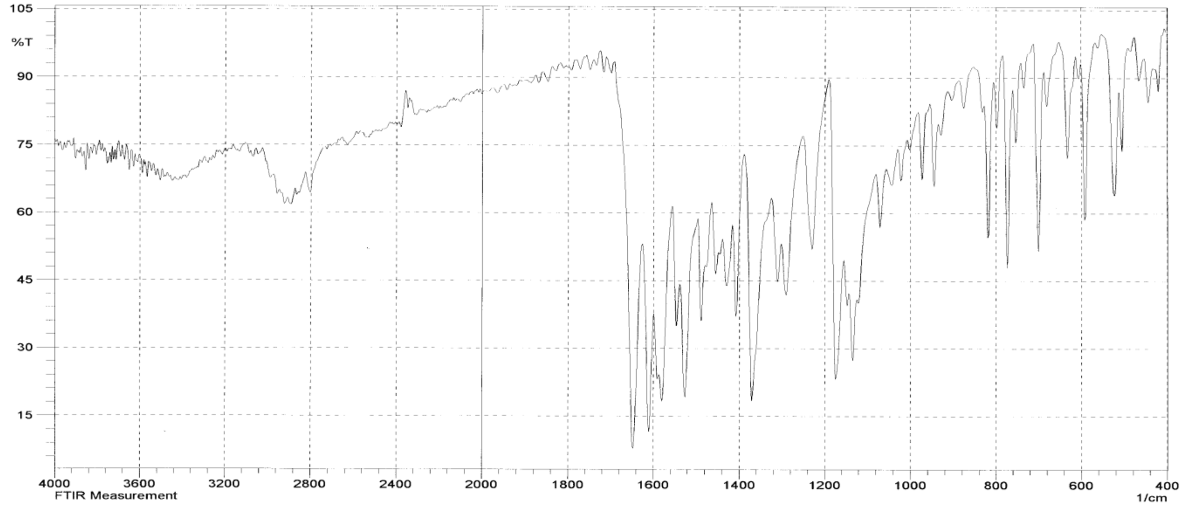


Figure 8: FT-IR spectrum of Schiff base(II) ligand

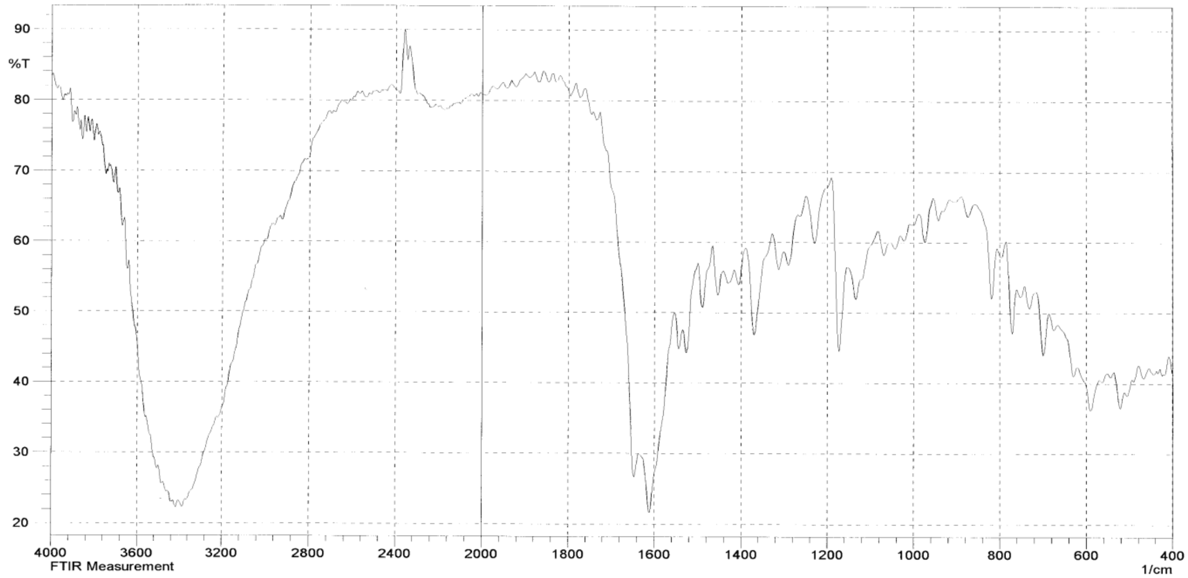


Figure 9: FT-IR spectrum of Mn-complex

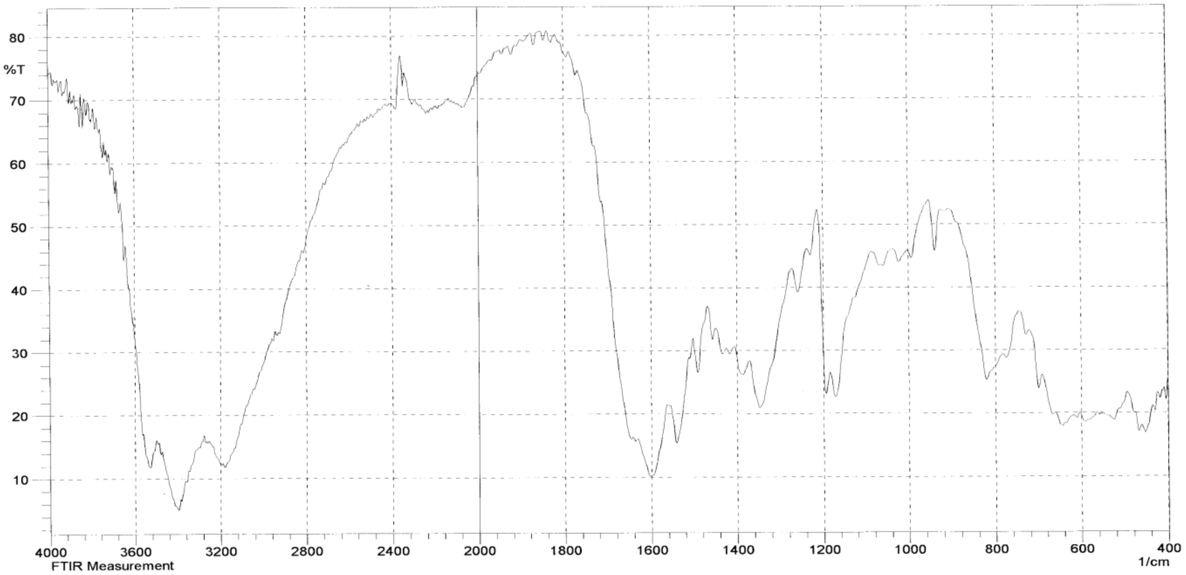


Figure 10: FT-IR spectrum of Co- complex

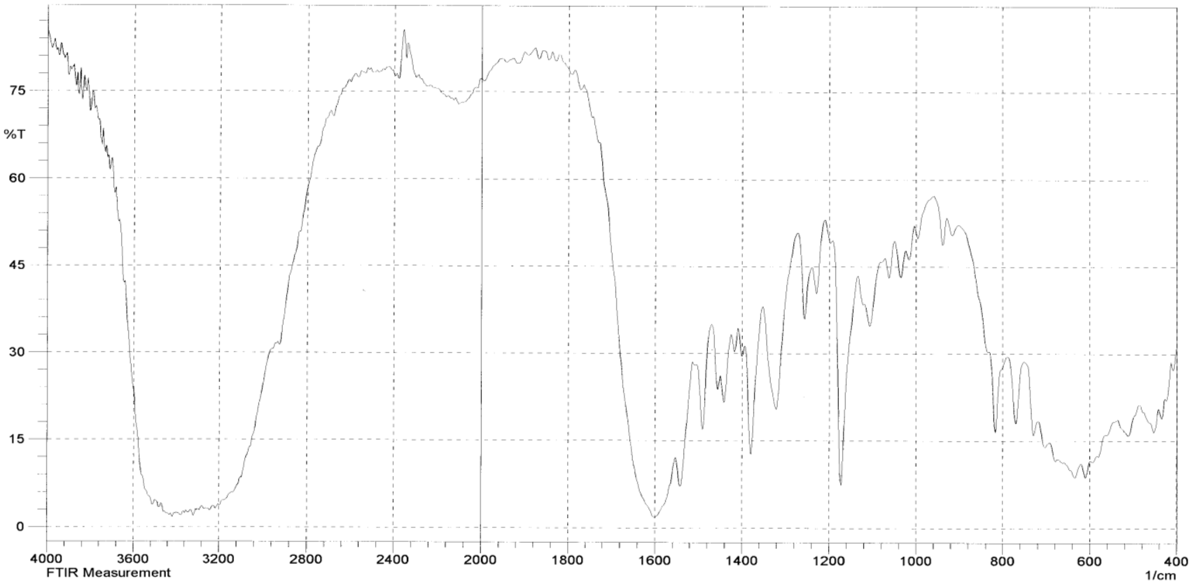


Figure 11: FT-IR spectrum of Ni - complex

4.CONCLUSION

This paper report the preparation and identification of bis 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 12**.

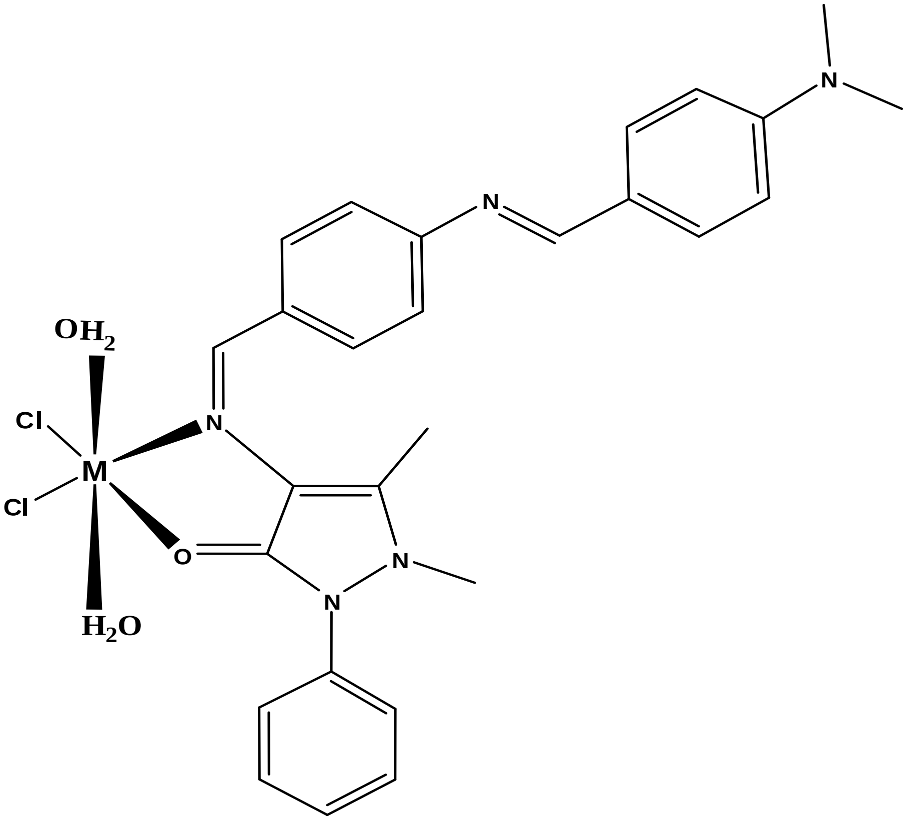


Figure 12: The proposed structural formula of Mn(II),Co(II) and Ni(II) with Schiff base(II) ligand

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