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Research Paper

Cobalt (II) and Nickel (II) Complexes with Schiff Base Ligand Derived From 4-Amino Antipyrine: Synthesis, Spectral, Characterization and Thermal Studies

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Abstract

Metal complexes of the Schiff base ligand, synthesized via condensation p-dimethylamino benzaldehyde with Bis (4-aminoantipyrine) benzene 1, 4-diamine which has synthesized from condensation 1, 4-phenylene diamine and 4-aminoantipyrine, are synthesized from chloride salts of Co (II) and Ni(II) with ligand in ethanol. The metal complexes and ligand are characterized on the basis of elemental analyses, melting point, molar conductance, UV –Visible, FTIR and thermogravimetric analysis. The molar conductance data reveal that the metal chelates of the ligand with Co (II) and Ni (II) are electrolytes. The present results suggested that the Schiff base ligand as tetradentate is coordinated with metal ions through the four nitrogen atoms.

Keywords: *4-aminoantipyrine, Cobalt, Nickel, tetradentate, TGA.*

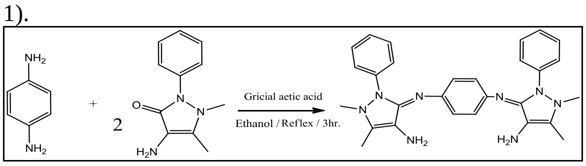
1. Introduction

Bis Schiff bases are the organic compounds containing two azomethine group (-HC=N-) which coordinator from through it with a metal ion (Zayed et al.,2018). These compounds form the condensation of a compound containing amine groups with a carbonyl compound may be aldehyde or ketone under a specific condition (Vlad et al.,2018). It has been shown that many of the Schiff bases compounds are catalytic in many different interactions (Gupta, 1. K. , and Sutar, A. K. 2008). There have been many studies on their applications in homogeneous and heterogen -eous catalysis (Liu,X.,2018). The thermal stability of many Schiff base complexes was useful for applying them as catalysts in high-temperature reactions (Das, P.,and Linert,W.,2016). Bis Schiff bases and their complexes are widely used for industrial purposes (Gupta, N. K.,2016) and also exhibit a broad range of biological activities including antibacterial (Abu-Dief, A. M., and Nassr,L.A.2015), antifungal (Shiju., 2015), antiproliferative (Arunadevi, A., and Raman, N. 2018), antimalarial (Manjula,B.,et al 2014).,anti-inflammatory (Shah,S.,Vyas,R., and Mehta, R. H. 1993) and antipyretic properties (El-Sonbati,A.Z.,2013). The present study describes the coordination behavior of bis Schiff bases bis (4-(4-(dimethylamino) benzylidene-antipyrine-benzene- 1,4-diamine) towards Co(II) and Ni(II) metal ions. Their spectral properties and thermal behavior have been investigated.

2. Materials And Methods

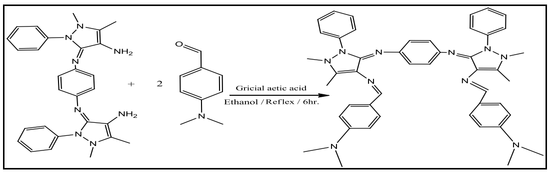
All chemicals used were of highest purity and without further purifications ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$) from Riedeal-Dehaenage, para methylene diamine, dimethyl amino benzaldehyde and 4-aminoantipyrine were obtained from BDH, methanol and ethanol from Fluka. Microanalysis of carbon, hydrogen and nitrogen were btained using by Perkin Elmer CHNS/O- analyzer 2400, The absorbance spectrum were recorded in the range of 250–900 nm using UV-Vis. Spectrophotometer model Shimadzu UV-Vissible 1700 spectrophotometer. The infrared spectra of the ligand and the obtained complexes were recorded using KBr discs on FT-IR 8000 Shimadzu in the range of (400-4000)cm^{-1}. Thermal analysis (TGA) carried out by Perkin Elmer TGA-FTIR (USA). 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.

Synthesis of Schiff base(I) (BAPB): 20 mL absolute ethanol solution of para methylene diamine (1.08 g, 0.01 mol) was added to 20 mL absolute ethanol solution of 4-aminoantipyrine(4.06g/0.02 mol) in the presence of five drops of glacial acetic acid as a catalyst. The reaction mixture was refluxed for two hours. The resultant solution was cooled to room temperature. The yellow precipitate of bis(4-aminoantipyrine)benzene 1,4-diamine was formed which was filtered and recrystallized in absolute ethanol(scheme-1).



Scheme1: The synthesis of (BAPB)

Synthesis of Schiff base ligand (BDBAD): In ethanol solution of bis (4-aminoantipyrine) benzene 1,4-diamine (4.78 g, 0.01mole, 20 mL) was taken in a burette and added dropwise to the ethanolic solution of para dimethylamino benzaldehyde (2.98 g, 0.02 mol, 20 mL), Add five drops of glacial (CH_3COOH) with constant stirring for three hours (Saritha Reddy et al., 2011). The dark yellow precipitate compound (II) was then obtained by filtration and recrystallized from hot ethanol, and dried over $CaCl_2$ (scheme-2).



Scheme 2: synthesis of (BDBAD) ligand

Synthesis of Schiff base complexes: The mixtures of the (BDBAD) under investigation (7.4 g, 0.01 mol) in 30 mL ethanol and metal salts $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ (2.37 g, 0.01mol) in the same amount of the same solvent were refluxed for two 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 $CaCl_2$ under vacuum.

3. Results and Discusion

Prepared compounds are found to be solids soluble in ethanol and most common organic solvents such as chloroform, acetone, acetonitrile and dimethyl sulfoxide. In Table-1 shows the analytical results of some measured physical properties of prepared compounds and elemental analysis Indicates that all the complexes were in good agreement with calculated values of the proposed formula. The low value of molar conductivity observed in ethanol refers to the non-electrolyte and non-ionic structure behavior of the complexes (Kettle 1975).

Electronic spectra study: The absorption spectra of (BAPB), (BDBAD) ligand and its complexes were studied (Pallikavil, R.,et al 2012). The wavelength for the maximum absorption (λ_{max}) of the (BAPB) was found at 356 nm while the (λ_{max}) of (BDBAD) ligand was found at 349 nm. The spectra of metal complexes were recorded within the wavelength range (239–349)nm. Two absorption bands appeared for the (BAPB) at 249 nm which referred to the ($\pi\rightarrow\pi^*$) transitions of benzene ring while the band at 356 nm assigned to ($n\rightarrow\pi^*$). The UV-visible spectra of the (BDBAD) ligand showed two bands at 242nm and 349 nm assigned to ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) transitions within the molecule. The UV-Visible spectra of the complexes Co(II) and Ni(II) showed absorption peaks at (239,346 nm) and (241,342 nm) respectively, which were assign to ligand field and charge transfer transition(Lever 1968). The spectrum of the complexes shows relative change in the band's position compared to that of the ligand, as shown in Figure-1.

Table1: The physical properties of the prepared compounds

Molecular f	Elemental analysis, Found (Calc.) (%)			Molar con (ohm^{-1} cm^{2}. r $^{-1}$)	M. p. (°C	Yield(%)
	C	H	N			
$C_{28}H_{30}N$	70.27 (69.98)	6.32 (6.07)	23.41 (23.46)	-----	١٣٢	76
$C_{46}H_{48}N_{1}$	74.57 (74.42)	6.53 (6.41)	18.90 (19.04)	-----	164	66
$[Co(C_{46}H_{48}N_{10})Cl_2].H_2O$	63.45 (63.51)	5.56 (5.49)	16.09 (16.19)	68.8	197	68
$[Ni(C_{46}H_{48}N_{10})Cl_2].H_2O$	63.47 (63.36)	5.56 (5.45)	16.09 (16.01)	70.7	186	79

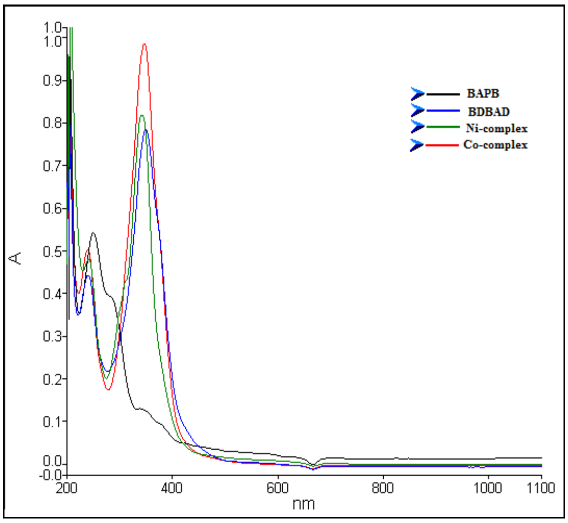


Fig.1: UV-Visible Spectra of the compounds

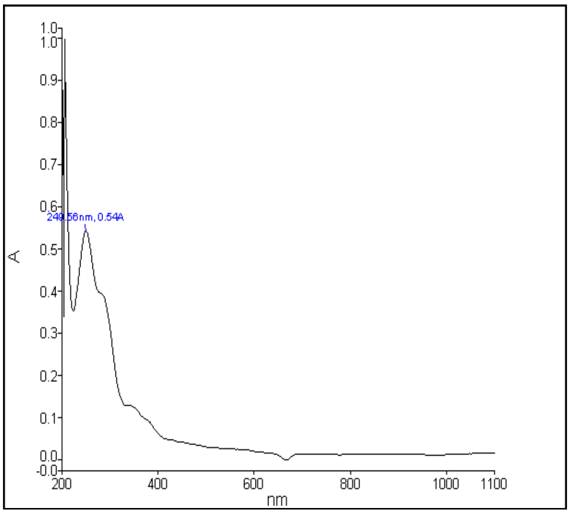


Fig. 2: Absorbance spectrum of (BAPB)

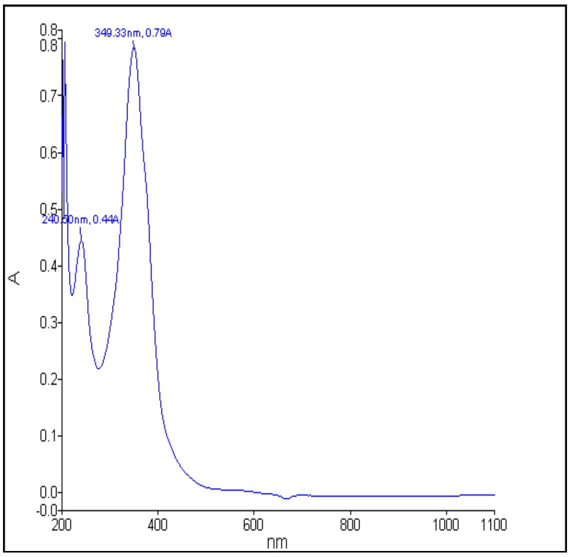


Fig.3: Absorbance spectrum of (BDBAD) ligand

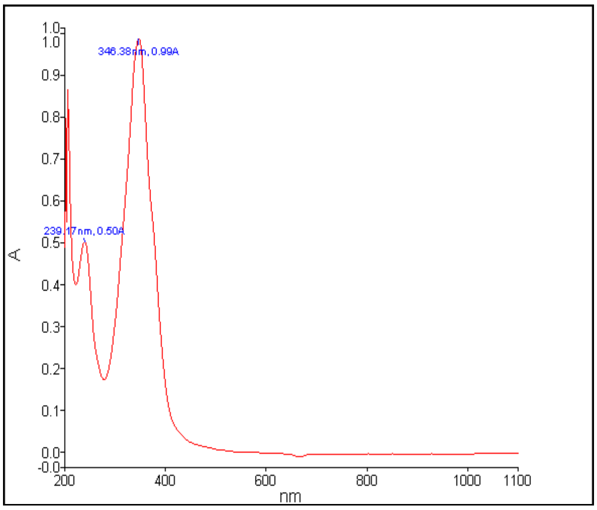


Fig.4: Absorbance spectrum of Co (II) Complex

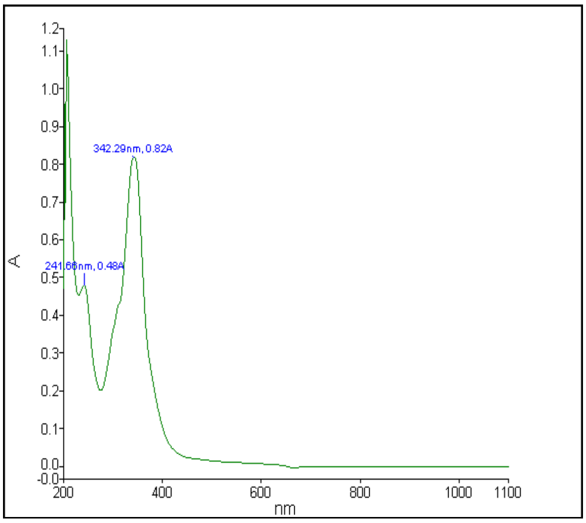


Fig.5: Absorbance spectrum of Ni (II) Complex

Infrared spectral study: The infrared spectra of the (BAPB), (BDBAD) ligand and the prepared Co(II), Ni(II) complexes have been compared, The obtained data are summarized in Table-2 with some assignments of the important characteristic bands. The data of the IR spectra were compared with each other in order to determine the participation of the coordinate sites and detect the changes that may have occurred. The absorption bands recorded within the range (1593-1656 cm-1) back to the existence of the azomethine ν(HC=N-) group. It refers to change in the frequency of this group to a lower frequency to the affected complexation (Geary 1971). The bands in IR spectra of the compounds at the ranges (1367-1525 cm-1) due to the bending frequency of (-CH3) and stretching vibration of (-C=C) (Silverstein 2005). The appearance of bands in the region of 456-506 cm-1 is tentatively assigned to (M-N) (Metal-Ligand) stretching bands. according to the results obtained, an octahedral structure has been tentatively suggested to these complexes.

Table 2: Some IR frequencies in (cm–1) of the prepared compounds

Comp.	*ν* (C-H)ar.	*ν* (C-H) alip.	ν(C=N)	ν(M-N)
$C_{28}H_{30}N_8$	3061w	2897	6s١٦٥	------
$C_{46}H_{48}N_{10}$	3085w	2987 2895	1649 s	------
$[Co(C_{46}H_{48}N_{10})Cl_2].H_2O$	3100 w	2920 2804	1593 s	522w 505w
$[Ni(C_{46}H_{48}N_{10})\ Cl_2].H_2O$	3162m	2920 2818	1593 s	505m

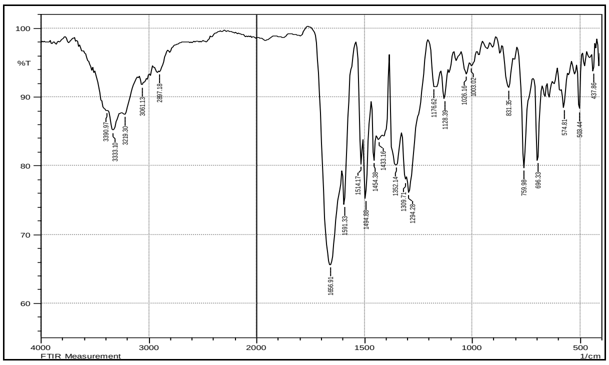


Fig. 6: FT-IR spectrum of (BAPB)

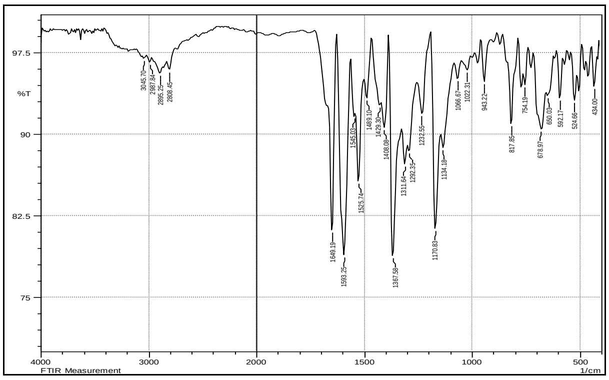


Fig.7: FT-IR spectrum of (BDBAD) ligand

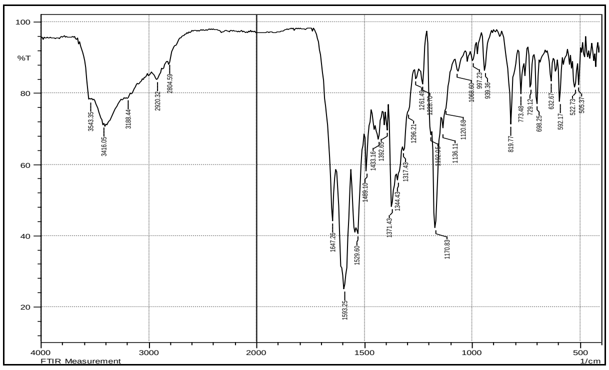


Fig.8: FT-IR spectrum of Co(II)-complex

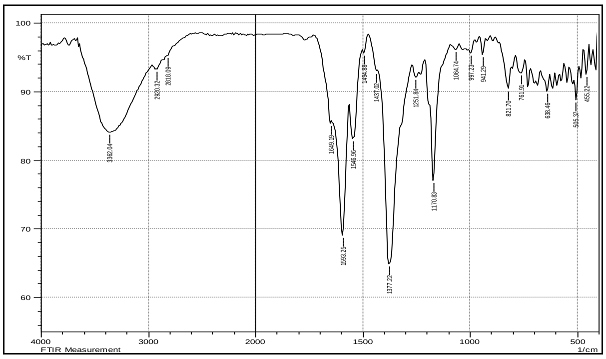


Fig. 9: FT-IR spectrum of Ni(II)- complex

Thermograph metric Analysis: TGA was carried out for solid (BDBAD) ligand and Co (II) complex under N2 flow. The heating rate was suitably controlled at 39.52°C min-1 and the weight loss was measured from the ambient temperature up to 905.9°C (El-Gammal et al., 2015). In general, the results of the analysis have been abridged in Table-3 indicating a good correlation between calculated and found weight loss values. The thermogram of (BDBAD) ligand exhibited three decomposition steps in the temperature range of 40–903.7°C. The first decomposition step in the temperature range of 39.52–353°C with % mass loss of 42.83% is assignable to the loss of (C18H22N4) molecules from the ligand.

The second and third decomposition steps with mass loss of 21.45% and 14.35% in the temperature range of 353-505°C and 505-903°C have considered the loss of remain organic ligand moiety. The TGA and DTG curve of Co(II) complex indicated that the compound was decomposed into three main steps after the water release step, from the start of running to 39.5-198.4°C, depending on a sample, with a corresponding endothermic DTA peak. After dehydration, the decomposition occurred in three steps, The first step involves the removal of Molecule (C18H22N4) (calculated 36.69%, found 46.07%) a temperature range of 198.4-452.7°C. The part of ligand (C9H11N6) was decomposed between temperature range 452.7-905.9°C (calculated 22.41%, found 24.48%) Which represents the second step. The third step has occurred at temperature higher of 905.9°C that suggested the completely decomposed and removed as Co/CoO and carbon residue (El-Ghar et al 2007).

Table 3: Thermal analysis of the prepared compounds by TGA and DTG

Comp.	TG range (°C)	step	TG mass		Re-main mass	explanation
			Found %	Calc. %		
$C_{46}H_{48}N_{10}$	39.5-353	1st	42.83	39.73	57.16	$C_{18}H_{22}N_4$ removed
	353-505	2nd	21.45	20.72	35.71	$C_{12}H_{14}N_2$ removed
	505-903	3rd	7.12	---	14.35	carbonation
$[Co(C_{46}H_{48}N_{10})Cl_2].2H_2O$	198.4 - 452.7	De-hyd. +1st	40.00	41.09	60.0	H_2O + $C_{18}H_{22}N_4$ removed
	452.7 -710	2nd	16.23	18.33	43.77	$C_{12}H_{14}N_2$ removed
	>710	3rd	8.26	----	35.51	Co/CoO Carbona-tion

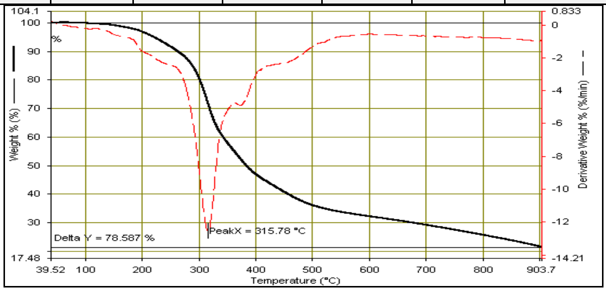


Fig. 10: TGA of (BDBAD) ligand

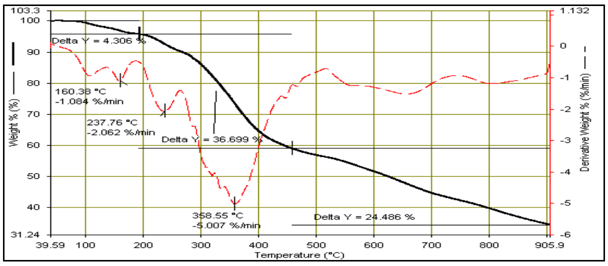


Fig.11: TGA of Co(II)-complex

4. Conclusion

The proposed geometry of the Co(II) complex is an octahedral while (Osowole 2008). According to these results, the structural formulas of these complexes may be proposed in Figure-2.

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