SYNTHESIS AND CHARACTERIZATION OF NEW SCHIFF BASE LIGAND WITH ITS SOME COMPLEXES DERIVED FROM 4-AMINO ANTIPYRINE, SULPHADIAZINE AND ACETOACETANILIDE

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ABSTRACT

The preparation of some new coordination compounds for cobalt (II), nikel (II), and copper (II) with Schiff base ligand derived from 4-Amino antipyrine, sulphadiazine and acetoacetanilide. Ligand (4- APSDA) were prepared and then react with metal salts in ethanol as asolvent in 1 : 1 ratio (metal : ligand). The complexes which have the general formula $[MLCI.2H_2O]$ where M = Co(II), Ni(II) and Cu(II). Ligand and its metal complexes were characterized using metal analysis by atomic absorption, infrared spectra, electronic spectra, ^1H NMR spectral studies, molar conductance and magnetic moment measurements. The measurements indicated that the ligand coordinate with the metal (II) ion in neutral tridentate manner through the azo methane nitrogen atoms, and oxygen group of the acetoacetanilide, stability constant of complexes were calculated by spectrophotometricaly. All the studies reveal a coordination six for the metals in all the complexes. Octahedral structures were suggested for metal complexes.

Key words: Schiff base, 4-amino antpyrine, Characterization, Metal chelate complexes.

INTRODUCTION

Amino heterocyclic compounds containig two or more potential donor centers play an important role in the study of competitive reactivity of an bidentate ligand system[1]. Heterocyclic phenazone and their derivatives (4-amino antipyrine) are know to act as bidentate or tridentate ligands when coordinated to metal ion[2]. Schiff base of 4-amino antipyrine and its complexes are know for their variety of application[3-5] i.e. in the areas of catalysis clinical application and pharmacologically[6-9]. Also the chemistry of antipyrine and its derivatives has been extensively investigated due to its physiological properties[10]. The study of the metal complexes of antipyrine in antineoplastic medication, molecular biology and bio engineering has become hotspots in recent years. This work describe the preparation new Schiff base and its some complexes derived from 4-amino antipyrine, sulphadiazine, and acetoacetanilide. The ligand is found to be chelating with metal ion in neutral tridentate manner through the azo methane nitrogen atoms and oxygen group of the acetoacetanilide.

EXPERIMENTAL

Materials

All the chemicals were supplied from BDH, and Fluka and used without further purification.
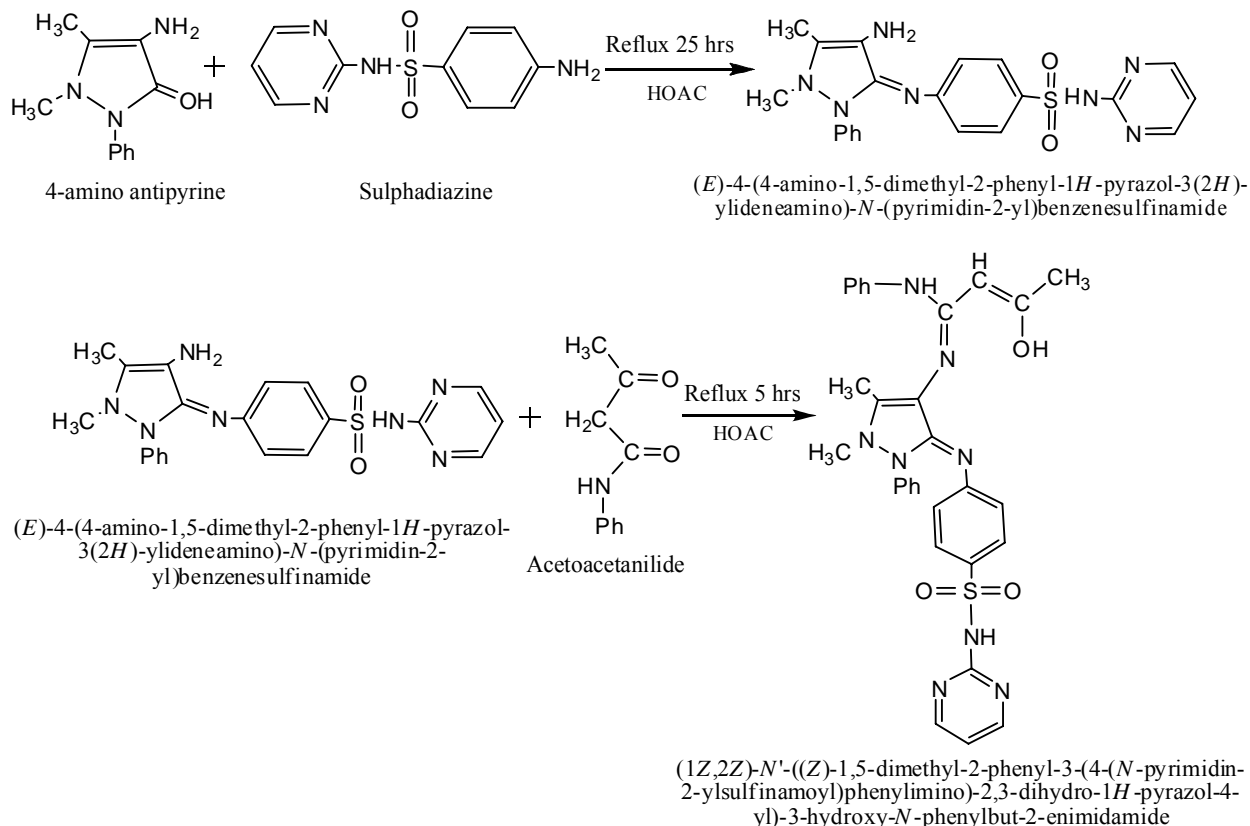
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Measurements

The melting point of ligand and its metal complexes were determined by Electro thermal melting point apparatus. Elemental analysis was performed by micro analytical unit of EA3000 A C.H.N Elemental analyzer Al-Albat University Jordan. FTIR spectra were recorded using (KBr pellets) 4000-400 cm^{-1} on FTIR testscan Shimadzu 8000 series. Electronic spectra were recorded in ethanol using Shimasdzu uv-vis 1700 spectrophotometer. The ^{1}H NMR spectra were obtained in DMSO solution using (Bruker, Ultra shield 3000 MKZ, Switzerland) spectrophotometer, The magnetic Susceptibility were measured on powder samples using Faraday method were made by Pascal constant[11].

Synthesis of Schiff base ligand (4-APSDA)

The method of preparation

The 4-amino antipyrine (2.03 g 0.01 mmol) dissolved in ethanol (40 cm^3) was mixed with sulphadiazine (2.50 g, 0.01 mmol) dissolved in ethanol (40 cm^3). To this solution added three drops from glacial acetic acid and the mixture was refluxed for 25 hrs. A clear coloured solution was obtained. The Schiff base ligand was isolated after the volume of the mixture was reduction to half by evaporation and recrystilized by hot ethanol. The crystalline product was dried over an hydrous CaCl$_2$. The Schiff base ligand ((E)-4-(4-amino-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-ylideneamino)-N-(pyrimidin-2-y1) benzene sulfinamide) has been taken and dissolved (4.35 g, 0.01 mmol) in (30 cm^3) of ethanolic solution with the same volume of ethanolic solution of (acetoacetanilide) (1.77 g, 0.01 mmol). To this mixture was added three drops from glacial acetic acid the mixture was refluxed with stirring for 5 hrs. The resulting solution was evaporation to half volume and precipitated product was collected by filtered off, purified by crystallization from hot ethanol, and dried over anhydrous CaCl$_2$. Yield : 62% : m.p.: 187°C (**Scheme 1**).

4-amino antipyrine   Sulphadiazine   (*E*)-4-(4-amino-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-ylideneamino)-*N*-(pyrimidin-2-yl)benzenesulfinamide

(*E*)-4-(4-amino-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-ylideneamino)-*N*-(pyrimidin-2-yl)benzenesulfinamide   Acetoacetanilide

(1*Z*,2*Z*)-*N'*-((*Z*)-1,5-dimethyl-2-phenyl-3-(4-(*N*-pyrimidin-2-ylsulfinamoyl)phenylimino)-2,3-dihydro-1*H*-pyrazol-4-yl)-3-hydroxy-*N*-phenylbut-2-enimidamide

Scheme 1: Synthesis of the ligand (4-ABSDA)

Synthesis of complexes

The Schiff base ligand (1 mmol) dissolved ethanol absolute (25 mL) was mixed with salts of Co (II), Ni(II), and Cu(II) ions (1 mmol) dissolved in ethanol (25 mL). The product was isolated after reduction of volume by evaporation. It was filtered off, washed with ethanol and dried under vacum. The complexes thus obtained are listed in Table 1.

RESULTS AND DISCUSSION

The new Schiff base ligand (4-APSDA) is orange crystals, but the prepared complexes of this ligand vary in colour depending of metal ion. The complexes are quiet air-stable in soluble in water, but its soluble in common organic solvents. Some pohesical and chemical propertied for Schiff base ligand and its chelate complexes with Co(II), Ni(II) and Cu(II) metal ions are listed in Table 1. In all cases (1 : 1) (metal : ligand) solid complexes are isolated, that is greement with the stoichiometric ratio found using molar ratio method. The complexes are non electrolytes. Attempts to propose the structure of the isolated complexes come for full in vestigation using the following studies.

Metal : Ligand ratio

The metal : ligand ratios of chelates were determined by the method of molar ratio method at the wave lengths of maximum absorption. The compound (4-APSDA) was found to form (1 : 1) chelates with metal ions under studies. These results are in agreement with the values reported for some Schiff base complexes[12].

Microanalysis

The elemental analysis data the complexes as shown in Table 1. It was found that the theoretical values are in good agreement with the found data. The purity of the Schiff base ligand were tested by TLC Technique and C. H. N elemental analyses.

Table 1: Physical data and analysis of the ligand and its complexes

| S. No.	Compd.	Color	M.P. ºC	Yied %	Formula	Found, (Calc.) %			
						C	H	N	M
1	Ligand	Orange	187	62	$C_{31}H_{30}N_8O_3S$	(62.62) 61.97	(5.05) 5.01	(18.85) 18.42	-
2	[CoLCl.2H$_2$O]	Green	208	78	[Co(C$_{31}$H$_{33}$N$_8$O$_5$S)Cl]	(51.67) 51.26	(4.58) 4.32	(15.55) 15.51	(8.18) .06
3	[NiLCl.2H$_2$O)	Brown	166	71	[Ni(C$_{31}$H$_{33}$N$_8$O$_5$S)Cl]	(51.68) 50.86	(4.58) 4.12	(15.56) 14.98	(8.15) 8.01
4	[CuLCl.2H$_2$O)	Green	140	68	[Cu(C$_{31}$H$_{33}$N$_8$O$_5$S)Cl]	(51.34) 51.21	(4.55) 4.47	(15.46) 15.10	(8.76) 8.62

Infrared spectra

In order to study the the binding mode of the Schiff base to the spectra of the complexes, the data are given in Table 2. The O-H stretching and bending vibration frequencies acetoacetanilide moiety of the ligand appearing in the region (3500-3335 cm^{-1}) and (1310 cm^{-1}), respectively indicate that enolic carbonyl group is not involved in the reaction and only the imide carbonyl group participates in the condensation[13].

The disappearance of these two peaks in the spectra of all the complexes the indicates that the chelation takes place via the enolic -OH group. Both the ligand and the complexes shows an intense beak at (3227) cm^{-1}, which is a characteristic feature of the (-NH) stretching frequency, indictating the existence of free (-NH) group[14]. The ligand shows its characteristic (-C=N-) band at (1653) cm^{-1}, which are also shifted to lower frequencies in the spectra of the complexes (1635-1640) cm^{-1} [6,15]. The spectrum of free ligand show two absorption bands at (1321) cm^{-1} and (1158) cm^{-1} due to symmetrical and asymmetrical vibration of (O=S=O) group[16]. These bands are stable in position and intensity in free ligand and its metal complexes. The all complexes shows abroad band at (3000-3550) cm^{-1} that suggests that water is corrdinated to the central metal ion[13]. Also the complexes show an intense peak at (842) cm^{-1} may be attributed to rocking and wagging modes of coordinated water[17,18]. The spectra of chelate complexes showed new weak bands in the region (570-406) cm^{-1}. These bands did not present in the spectrum of ligand may be attributed to vibration (M-O) and (M-N) provide evidences of the bonding of oxygen and nitrogen metal ions[19]. Repesentative example of their spectra given in Fig. 1.

**Table 2: IR spectra frequencies for the ligand and its metal complexes in cm^{-1}**

Compound	v (N-H)	v (C=N)	v (O=S=O)	v (M-N)	v (M-O)
Ligand (4-APSDA)	3227	1653	1324, 1158	-	-
[CoLCl.2H$_2$O]	3223	1620	1325, 1157	570	412
[Ni LCl.2H$_2$O]	3226	1635	1323, 1155	570	406
[Cu LCl.2H$_2$O]	3221	1638	1324, 1157	570	412
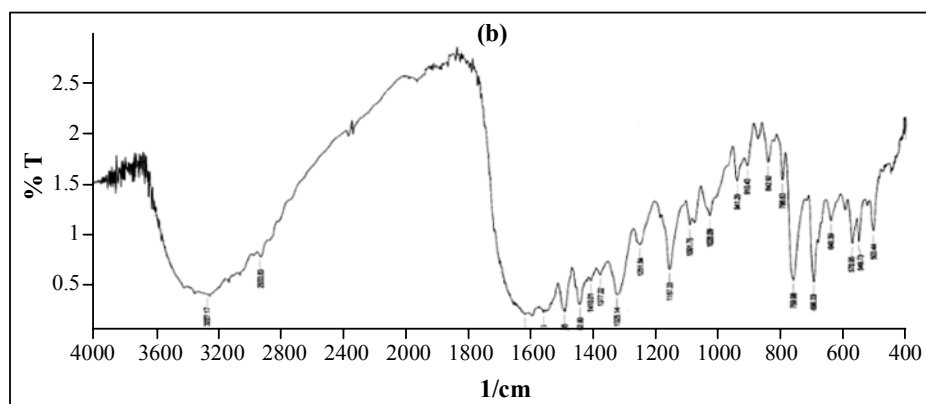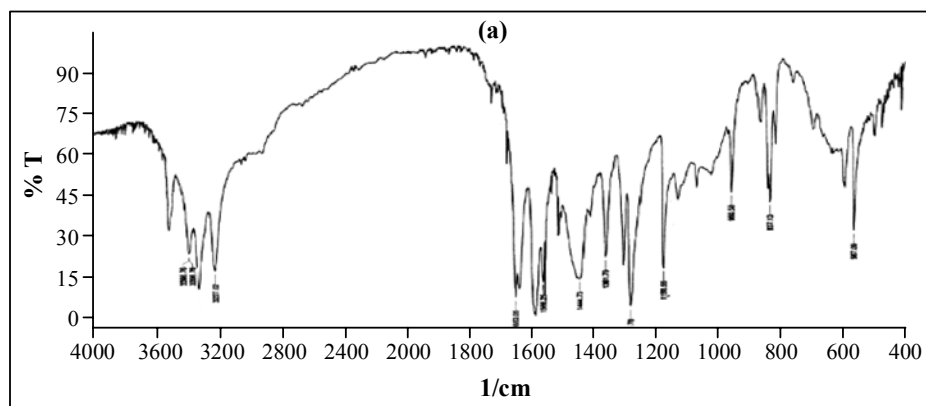
Fig. 1: IR spectra of (a) the ligand (4-APSDA) & (b) [CoLCl.2H$_2$O]

Magnetic preparation and electronic spectra

The spectral data and the magnetic moment of prepared complexes are listed in Table 3 Fig. 2 show the spectra of ligand and cobalt complex.
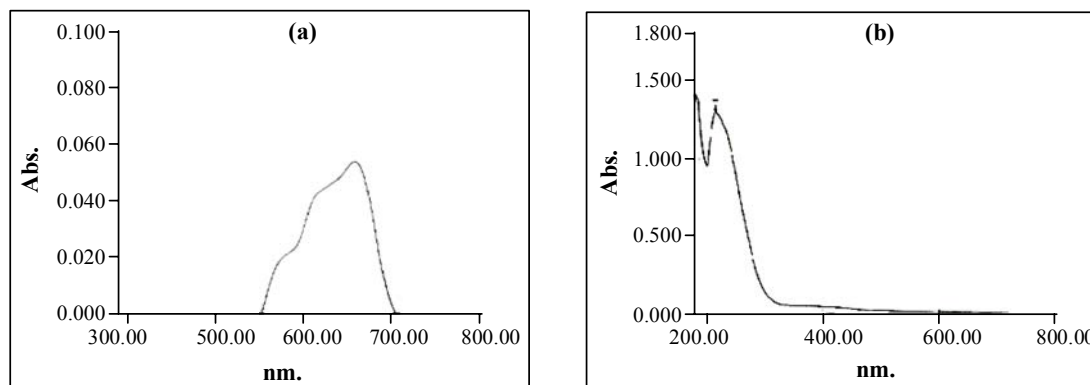
Fig. 2: Electronic spectrum of (a) the ligand (4-APSDA) & (b) [CoLCl.2H$_2$O]

Ligand spectrum: The electronic spectronic spectrum of free Schiff base showed two band at (307 nnm, 3253 cm^{-1}) and (274 nm, 36496 cm^{-1}) dueto $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transition[20].

Cobalt (II) complex: The magnetic moment value of the Co(II) (d7) complex is (5.12 B.M)[21]. The electronic spectrum of this complex show bands at (656 nm, 15243 cm^{-1}), (452 nm, 22123 cm^{-1}) and (380 nm, 26315 cm^{-1}) be assigned to 4T$_{1g}$ $\rightarrow$ 4T$_{2g}$ (F), 4T$_{1g}$ $\rightarrow$ 4A$_{2g}$ (F), and 4T$_{1g}$ $\rightarrow$ 4T$_{1g}$ (P), respectively[22]. The spectrum resemble those reported for octahedral complexes[23].

Nikel (II) complex: The magnetic moment for the complexes of Ni(II) (d8) was found to be (3.16 B.M), which is with the range of octahedral Ni(II) complexes[24]. The electronic spectrum of this complexes show bands at (743 nm, 13458 cm^{-1}) and (686 nm, 14577 cm^{-1}) which can be assigned to 3A$_{2g}$ $\rightarrow$ 3T$_{1g}$ (F), and 3A$_{2g}$ $\rightarrow$ 3T$_{1g}$ (F), respectively[8].

Copper (II) complex: The magnetic moment value of the Cu(II) (d9) complex (1.61 B.M) this value indicate with in the expected for one electron, and d-d spectrum of this complex. Band at (554 nm, 18050 cm^{-1}), which may assigned to 2E$_g$ $\rightarrow$ 2T$_{2g}$ transition in an approximately octahedral environment[20,25].

^{1}H NMR spectra

The ^{1}H NMR spectrum of the Schiff base in DMSO shows the following signals –CH aromatic at (6.9-7.8) δ range, pH NH at 4.1 δ and =C-CH at 6.3 δ, N-CH$_3$ at 3.3 δ, -CH pyrmidine at 8.3 δ, The peak at 11.8 δ is attributed to the enolic –OH group present in the acectoacetanilide moiety. The absence of this peak, noted in the complexes, indicates the loss of the –OH proton due to complexes ion. These is no appreciable change in all other signals in this complexes.

Conductivity measurement

All chelate complexes prepared in this work showed values ranged between (3-6) S.mol^{-1}.cm^2 in DMSO at room temperature these vales indicating that lower conductivity of the complexes[12,26].

Calculation of the metal complexes stability constant Chelate stability constant are determined spectropotometrically by measuring the absorbance of mixture solutions of both metal and ligand, wavelength λ$_{max}$. The degree of formation of the complexes were calculated base on the relationship β = (1-α)/(α2c) for 1 : 1 metal complexes and α = Am – As/Am. Where Am and Asare the absorbance's of the fully

and partially formed chelate complexes, respectively. The calculated (log β) values of these complexes are listed in Table 3.

Table 3: Electronic spectra, molar conductance and magnetic moment, stability constant values of complexes

| Compound	Absorption bond (nm, cm⁻¹)	Transition	Conductivity $S.mol^{-1}.cm^{-1}$	M_{eff} B.M.	β	Log β
Ligand (4-APSDA)	307 nm (32573 cm⁻¹) 274 nm (36496 cm⁻¹)	$\pi \rightarrow \pi$ $n \rightarrow \pi^*$	-	-	-	-
[CoLCl.2H₂O]	656 nm (15243 cm⁻¹) 452 nm (22123 cm⁻¹) 380 nm (26315 cm⁻¹)	$^4T_1g \rightarrow {}^4T_2g$ (F) $^4T_1g \rightarrow {}^4A_2g$ (F) $^4T_1g \rightarrow {}^4T_1g$ (P)	6	5.12	$6.2445*10^4$	4.79
[NiLCl.2H₂O]	743 nm (13458 cm⁻¹) 686 nm (14577 cm⁻¹)	$^3A_2g \rightarrow {}^3T_1g$ (F) $^3A_2g \rightarrow {}^3T_1g$ (F)	3	3.16	$4.705*10^4$	4.67
[CuLCl.2H₂O]	554 nm (18050 cm⁻¹)	$^2Eg \rightarrow {}^2T_2g$	5	1.61	$8.788*10^4$	4.94
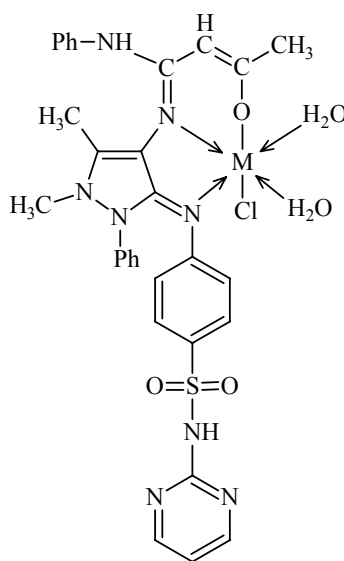
M=Co(II), Ni(II) and Cu((II)

Fig. 3: The proposed structural formula of the metal chelate complexes

(a)   (b)
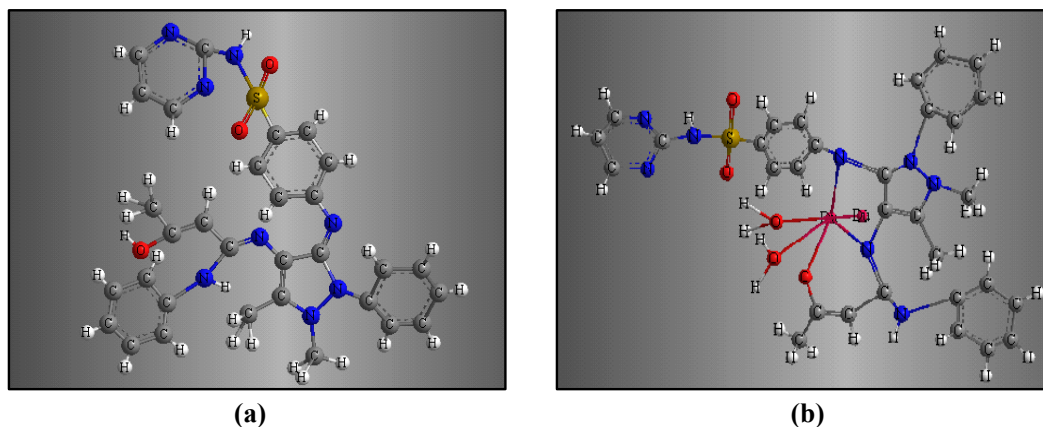
Fig. 4: Moleculer structure of (a) The ligand (4-APSDA) & (b) of the metal chelate complexes
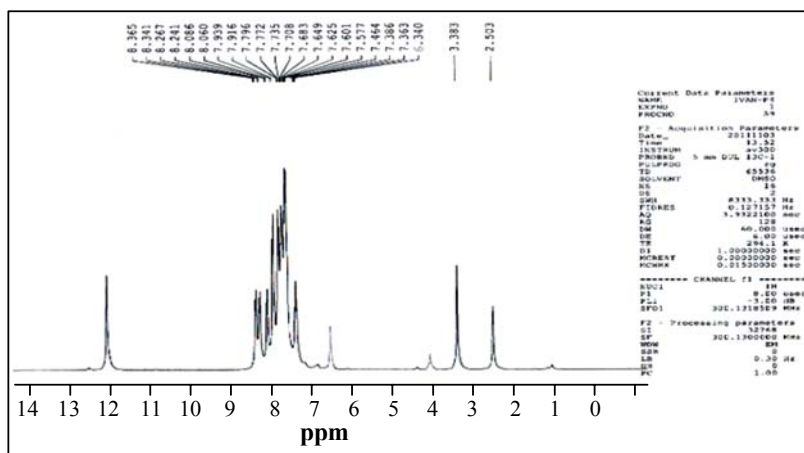
Fig. 5: **¹HNMR spectrum of the ligand (4-APSDA)**

CONCLUSION

This paper reports that:

- The ligand (4-APSDA) behaves like mono basic tridentate manner, by coordination with Co(II), Ni(II) and Cu(II) metal ions.

- All the complexes an stable and non ionic.

- All the proposed geometry of the complexes are octahedral. According to these results the structural formulas of these complexes may be proposed as in Fig. 3

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