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Metal Complexes of Schiff Base Derived from Terephthalaldehyde and 2-Amino-5-Ethyl-1,3,4-Thiadiazole Synthesis, Spectral and Thermal Characterization

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Metal Complexes of Schiff Base Derived from Terephthalaldehyde and 2-Amino-5-Ethyl-1,3,4-Thiadiazole Synthesis, Spectral and Thermal Characterization

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The present study deals with the preparation of Schiff base and its chelates with some transition metal ions, e.g., Co(II), Ni(II), Cu(II) and Fe(II). The structures of the ligand N-(5-ethyl-1,3,4-thiadiazole-2-yl)terephthalaldehyde imine (L) and its complexes have been synthesized and characterized by IR, ^{1}H-NMR spectra, elemental analyses, magnetic susceptibility, UV-vis and thermogravimetry-differential thermal analysis (TGA-DTA). From the magnetic moment and UV-vis spectra data, it is found that the geometrical structures of these complexes are octahedral.

Keywords metal complexes, spectroscopy, transition metal compounds

INTRODUCTION

During the last two decades, many kinds of compounds of substituted 1,3,4-thiadiazoles, which have special structures and properties have been widely reported in the field of synthesis, spectroscopic analysis and traditional application of medicine and pesticide.[1]

The thiadiazole ring is associated with diverse biochemical activity probably by virtue of incorporating a toxophoric —N=C—S— linkage, the importance of which has been well-stressed in many pesticides. Actually various 2-amino/substituted-amino-1,3,4-thiadiazoles and their Schiff bases have recently received significant importance because of their diverse biochemical properties.[2] As a ligand, it also provides many potential binding sites for complexation of diverse metal ions (such as Co(II), Ni(II), Cu(II) or Zn(II) among others) with well established biological roles.[3]

In this study, we report the synthesis, spectral, and thermal characterization of a novel Schiff base ligand (L) containing a ring of the thiadiazole and its Co(II), Ni(II), Cu(II) and Fe(II) complexes. Thus, in view of this, it has been considered of interest to study a complex containing the thiadiazole moiety.[1] ^{1}H-NMR spectra was obtained to determine the structure of the Schiff base ligand. The preparation and structure of the ligand showed as in Figure. 1.

RESULTS AND DISCUSSION

The ligand (**L**) was obtained by condensation of 2-amino-5-ethyl-1,3,4-thiadiazole (**1**) with terephthalaldehyde and was checked by IR, ^{1}H-NMR spectra, and microanalytical data (Table 1). Co(II), Ni(II), Cu(II) and Fe(II) complexes of ligand were air stable and prepared by the stoichiometric reaction of the corresponding metal(II) chloride with the Schiff base ligand, in molar ratio M:L of 1:1, 2:1, 1:2 and 1:2, respectively. The analytical data are in good agreement with the proposed stoichiometry of the complexes. All the complexes are soluble in common organic solvents such as methanol, acetone, chloroform and DMF.

According to the elemental analyses, IR, UV-vis, magnetic susceptibility and thermogravimetric analyses results, the structures of complexes are suggested to be as shown in Figures 2–5. The characterization data of ligand and its complexes are given in Tables 1–4.

Infrared Spectra

The IR spectral bands of the ligand and its complexes are listed in Table 2 together with assignments for most of the important peaks. The position and/or the intensities of these peaks are expected to be changed upon chelation.

In the IR spectrum of (**1**) characteristic peaks are at 3287 cm^{-1} $\upsilon(NH_2)_{as}$, 3108 cm^{-1} $\upsilon(NH_2)_s$ and 1536 cm^{-1} (N—H) out of plane bending vibrations.[4] There is no N-H band in the IR spectra of ligand.[5,6]

IR spectra of the Schiff base reported here showed the absence of bands at ≈1700 and 3287, 3108 cm^{-1} due to carbonyl

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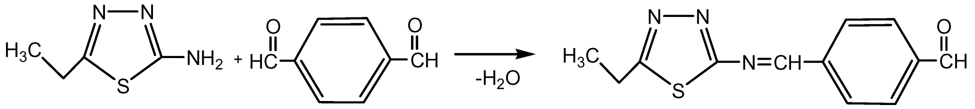

FIG. 1. Synthesis of the ligand : N-(5-ethyl-1,3,4-thiadiazole -2-yl) terephthalaldehyde imine (L).

υ(C=O) and $\upsilon(NH_2)$ stretching vibrations (present in the starting materials) and the appearance of a strong new band at 1629 cm^{-1} assigned as azomethine υ(C=N) vibration.[7]

The spectra of the free ligand display band at 1692 cm^{-1} due to υ(C=O). The position of υ(C=O) is found to be dependent on the electronic nature of the p-substituents.[8] The υ(C=O) stretching vibration that is useful for diagnosis of coordination located at 1692 cm^{-1} for ligand remain at the same position as in ligand, indicating that the υ(C=O) group does not coordinate with the metal atoms[4]

The solid state IR spectra of the complexes compared with those of the ligand indicate that the C=N band 1629 cm^{-1} is shifted to lower values for complexes Co(II), Ni(II), Cu(II) and Fe(II). The phenomenon appears to be due to the coordinated of azomethine nitrogen to the metal ion.[9]

The spectra of all complexes exhibited intense broad 3505–3300 cm^{-1} due to υ(OH) of hydrate and coordinated water or ethanol molecule.[10] The presence of hydrate or/and coordinated water molecules or ethanol molecule are also confirmed by elemental analyses and thermogravimetric analyses.

The infrared spectra of the ligand show bands 1629 and 1498-1444 cm^{-1}, which may be assigned to be υ(C=N) (azomethine group) and υ(>C=N—N=C<) (ring), respectively. The first band is shifted towards the lower frequency region (22 cm^{-1}) in the Fe(II) complex indicating the coordination of the azomethine nitrogen atom of the Schiff base. However the second band υ(>C=N—N=C<) (ring) is found to split into two; one almost located at the original position indicating non-coordinated at the υ(C=N), and other shifted two lower frequency 1430 cm^{-1}, arising due to coordinated υ(C=N) mode. The splitting of the υ(>C=N—N=C<) (ring) absorption band suggests that only one of the ring nitrogen is involved in coordination and other is free and non-coordinated. This is further supported by a new band at 470 cm^{-1} assignable to υ(M-N) in the complex. The υ(C—S—C) band in the ligand occurs at 770 cm^{-1}, which remains unaltered in the spectra of the complex indicating the non-coordination of sulphur atom of the thiadiazole ring.[11]

In the spectra Co(II) and Cu(II) complexes the υ(>C=N—N=C<) (ring), υ(N—N) vibrations remain almost unchanged indicating, thereby, non-involvement of the ring nitrogen in coordination. The υ(C—S—C) undergoes a negative shift in the complexes indicating the coordination of ring sulphur. The coordination through the azomethine nitrogen and sulphur is further supported by the occur of new bands at 471, 460 cm^{-1} in the spectra of the complexes which may be assigned to υ(M-N), respectively.[12] The IR spectra of Co(II) and Cu(II) complexes display an additional new bands at 330 cm^{-1}, assigned to υ(M-S).[13] In the IR spectrum of the complexes (M-S) bands could not be observed, that we study in 4000–400 cm^{-1} range.

In the Ni(II) complex the υ(>C=N—N=C<) (ring), υ(N—N) vibrations shifted to lower frequencies at 1460–1434 and 1050–943 cm^{-1}, arising due to coordinated ring nitrogen. The band at 772 cm^{-1} assigned to the thiadiazole ring υ(C—S—C) vibration is also shifted to lower frequency by ≈10 cm^{-1}, which is indicative of the involvement of the thiadiazole ring sulphur

TABLE 1
The colors, formula, formula weight, yields, melting points, magnetic moments and elemental analysis results of the ligand (L) and the complexes

Compounds	FW (g/mol)	M.p. (°C)	Yield (%)	μ_{eff} (B.M.)[a]	Elemental analyses/(%) calculated (found) C	H	N	S
Ligand (orange) $C_{12}H_{11}N_3SO$	245	170	60	–	58.76 (58.72)	4.49 (4.22)	17.14(17.20)	13.06 (13.32)
$[CoL(H_2O)_4].2Cl.H_2O$ (Dark red) $C_{12}H_{21}Cl_2CoN_3SO_6$	464.84	210	48	4.11	30.98 (31.31)	4.52 (4.88)	9.04(9.18)	6.88 (6.83)
$[Ni_2LCl_4(H_2O)_4].4H_2O$ (Pale red) $C_{12}H_{27}Cl_4Ni_2N_3SO_9$	648.24	250	54	2.59	22.21 (21.55)	4.16 (3.87)	6.48(6.18)	4.94 (4.64)
$[CuL_2Cl_2].2H_2O$ (Pale green) $C_{24}H_{26}Cl_2CuN_6S_2O_4$	660.46	235	58	1.07	43.61 (43.43)	3.94 (4.20)	12.72(12.60)	9.69 (10.11)
$[FeL_2Cl_2].EtOH$ (Dark red) $C_{26}H_{28}Cl_2FeN_6S_2O_3$	662.75	225	55	4.73	47.08 (47.00)	4.22 (4.25)	12.67(12.30)	9.66 (9.72)

[a] Magnetic moment at 30°C.

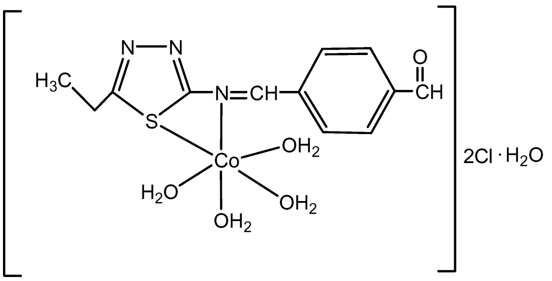

FIG. 2. Suggested structure of the octahedral Co(II) complex of the ligand (L).

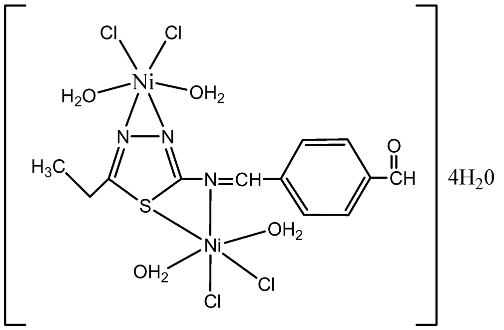

FIG. 3. Suggested structure of the octahedral Ni(II) complex of the ligand (L).

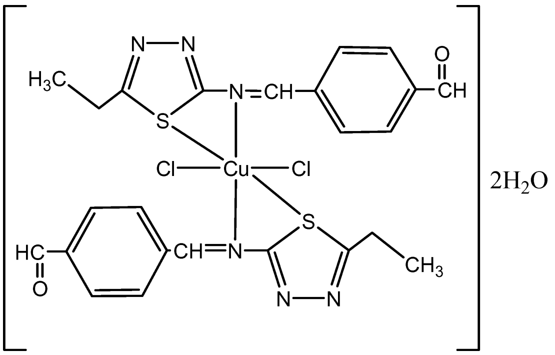

FIG. 4. Suggested structure of the octahedral Cu(II) complex of the ligand (L).

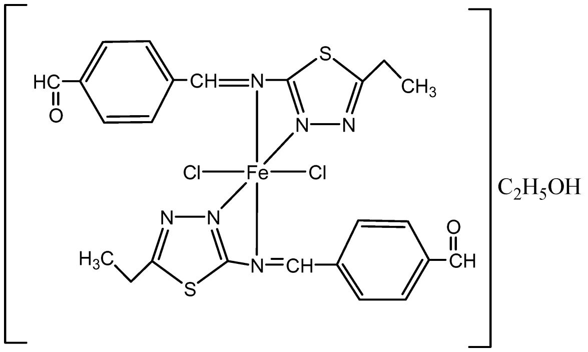

FIG. 5. Suggested structure of the octahedral Fe(II) complex of the ligand (L).

in chelation. Further evidence of the metal ions was shown by the appearance of weak low frequency new bands 529 and 460 cm^{-1}, which can be assigned for υ(M-N) and υ(M-O). The IR spectra of Ni(II) complex display an additional new bands at 360–365 cm^{-1}, assigned to υ(M-S).[13,14] In the IR spectrum of the complexes (M-S) bands could not be observed, that we study in 4000–400 cm^{-1}.

These new bands were observable only in the spectra of the metal complexes and not in the spectra of the uncomplexed Schiff base and thus confirm the participation of these heteroatoms (N, O or S) in the coordination.[15]

In the spectra Co(II) and Ni(II) complexes, the IR bands at 894-831 and 816 cm^{-1}, respectively, υ(H_2O) of coordinated water is an indication of the binding of the water molecules to the metal ions. New bands are found in the spectra of the complexes in the regions 513, 529 cm^{-1}, respectively, which are assigned to υ(M-O) stretching vibrations.[16]

In the Co(II) complex the chloride ions do not coordinate with the metal ions. In the CI^- test with $AgNO_3$, precipitation of white AgCI salt is immediately evident.

^{1}H-NMR Spectra

The ^{1}H-NMR spectrum of the free ligand (**L**) was run in dimethylsulfoxide (DMSO-d_6) solution using tetramethylsilane (TMS) as internal standart. All the protons of the ligand were found to be in their expected region. The conclusions drawn from these studies lend further support to the mode of bonding discussed in IR spectra. The number of protons calculated from the integration curves. The ^{1}H-NMR spectra of the free ligand showed a singlet at 10.10 ppm due to the aldehide proton, a singlet at 9.10 ppm due to the azomethine proton, the broad multiplet in the range 8.20–6.80 ppm due to the aromatic protons and aliphatic protons at 1.20, 3.40 ppm.[17,18] Since all the metal complexes are paramagnetic, their ^{1}H-NMR spectra could not be obtained.

Magnetic Susceptibility and Electronic Spectra Measurements

The UV-vis spectra of the ligand and the complexes were recorded in the DMF solution in the wavelength range from 200 to 1000 nm. The corresponding magnetic susceptibility and electronic spectra measurements are collected in Tables 1 and 3.

In the spectrum of the ligand (**L**), the bands 350–390 nm range are assigned to the $n \rightarrow \pi^*$ transitions of the azomethine group and thiadiazole ring. During the formation complexes, these bands are shifted to lower wavelength, suggesting that the nitrogen atoms of the azomethine group and thiadiazole ring are coordinated to the metal ion. The values in the 300–350 nm range are attributed to the $\pi \rightarrow \pi^*$ transition of the aromatic and thiadiazole ring. In the spectra of complexes, these bands are shifted slightly to lower wavelength.[19]

The electronic spectra of the Co(II) complex shows two bands observed 505, 570 nm which may be assigned $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$

TABLE 2

Characteristic IR bands (cm^{-1}) of the ligand (L) and its complexes in KBr pellets

Assignment	Ligand	Co(II)	Ni(II)	Cu(II)	Fe(II)
υ(OH)	—	3400–3384	3373	3364	3480–3300
Aromatic υ(C—H)	3090–3082	3095	—	3090–3060	3186
Aliphatic υ(C—H)	2865–2806	2967–2923	2972–2865	2866–2806	2974–2850
υ(CH) —COH	2757	2754	2757	2757	2750
υ(C=O)	1692	1693	1687	1692	1690
υ(CH=N)	1629	1604	1610	1607	1607
υ(>C=N—N=C<)	1498–1444	1496–1440	1460–1434	1490–1440	1494–1430
υ(—N—N)	1045–980	1050–977	1050–943	1040–975	1044–952
υ(C—S—C)	772	765	762	766	770
υ(M—O)	—	513	529	—	—
υ(M—N)	—	471	460	460	470

and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively, and are of their octahedral geometry around the cobalt ion.[20] The magnetic susceptibility measurement (4.11 B.M.) for the solid Co(II) complex is also indicative of three unpaired electrons per Co(II) ion suggesting consistency with their octahedral environment.[21]

The electronic spectra of Ni(II) complex shows d-d bands in the region 544, 578-618, and 944 nm. These are assigned to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$,[21,22] respectively, consistent with its well-defined octahedral configuration. The proposed structure is supported by magnetic moment (2.59 B.M.) measured for the complex.

The electronic spectra of the Cu(II) complex shows a strong high-energy band at 315 nm and may be assigned to $^2B_{1g} \rightarrow {}^2E_g$transition.[23] The strong high-energy band, in turn, is assigned to metal → ligand charge transfer. The band observed at 431 nm is assigned to ligand → metal charge transfer band.[9] On the other hand, the Cu(II) complex shows an absorption band at 540 nm attributed to the $^2E_g \rightarrow {}^2T_{2g}$ transition, which is compatible with this complex having an octahedral structure. The proposed structure is supported by magnetic moment (1.07 B.M.) measured for the complex.

The electronic spectra of the Fe(II) complex has a magnetic moment value 4.73 B.M., which is consistent with two high spin octahedral geometry. The diffuse reflectance spectrum shows two absorption bands at 620 and 430 nm which are assigned to $^5T_{2g} \rightarrow {}^2E_g$ transition and charge transfer, respectively.[24]

Thermal Studies

The thermal stability of the ligand and its complexes were investigated by a combination of TGA and DTA. The TGA and DTA curves were obtained at a heating rate of 10°C/min. in a nitrogen atmosphere over the temperature range of 25–800°C. The thermal data are summarized in Table 4. The results obtained are in good agreement with the theoretical formula suggested from the elemental analyses. The weight losses for

TABLE 3

Electronic spectral data of the ligand (L) and its complexes (nm, ε) (in DMF)

Compounds	Wavelength in nm (ε)			
Ligand (L)	304–354, 390 (1400^a, 150) $\pi \rightarrow \pi^*$,n $\rightarrow \pi^*$	—	—	—
$[FeL_2Cl_2].C_2H_5OH$	307, 318 (175, 140) $\pi \rightarrow \pi^*$	324, 430 (125, 100) n $\rightarrow \pi^*$ L → M	620 (50) $^5T_{2g} \rightarrow {}^2E_g$	
$[CoL(H_2O)_4].2Cl.H_2O$	302, 360 (3000, 2600) $\pi \rightarrow \pi^*$,n $\rightarrow \pi^*$	505 (1000) $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	570 (500) $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
$[Ni_2LCl_4(H_2O)_4].4H_2O$	302, 370 (2300, 1300) $\pi \rightarrow \pi^*$,n $\rightarrow \pi^*$	544 (830) $^3A_{2g} \rightarrow {}^3T_{1g}(F)$	578–618 (2000, 1000) $^3A_{2g} \rightarrow {}^3T_{2g}(F)$	944 (500) $^3A_{2g}(F) \rightarrow T_{2g}(F)$
$[CuL_2Cl_2].2H_2O$	306 (750) $\pi \rightarrow \pi^*$	315 (250) $^2B_{1g} \rightarrow {}^2E_g$	431 (190) L → M	540 (25) $^2E_g \rightarrow {}^2T_{2g}$

ε = molar extinction coefficient (L mol^{-1} cm^{-1}), ^{a}maximum wavelength in 340 nm.

TABLE 4
Proposed decomposition steps and the respective mass losses of ligand (HL)-metal complexes

Equations	Temperature (°C)	% Loss in weight %Found(% calculated),	Decomp. products
$C_{12}H_{11}N_3SO$ [L]	25.50–115.16	—	Thermal stability
$C_{12}H_{11}N_3SO$	115.16–200.36	11.84 (11.85)	$-CH_2CH_3$
$C_{10}H_6N_3SO$	200.36–300.24	11.84 (11.85)	$-CHO$
$C_9H_5N_3S$	300.24– 620.88	34.29 (34.81)	$-C_2N_2S$
C_7H_5N	620.88–		
$[CoL(H_2O)_4].H_2O$			
$C_{12}H_{21}Cl_2CoN_3SO_6$	50.45–190.64	3.87 (3.70)	H_2O
$C_{12}H_{19}Cl_2CoN_3SO_5$	190.64–330.78	15.59 (14.81)	$4H_2O$
$C_{12}H_{11}Cl_2CoN_3SO$	330.78–370.16	15.25 (15.55)	2Cl
$C_{12}H_{11}CoN_3SO$	370.16–		
$[Ni_2LCl_4(H_2O)_4].4H_2O$			
$C_{12}H_{27}Cl_4Ni_2N_3SO_9$	60.85–100.98	11.85 (11.11)	$4H_2O$
$C_{12}H_{19}Cl_4Ni_2N_3SO_5$	100.98–276.42	10.37 (11.11)	$4H_2O$
$C_{12}H_{11}Cl_4Ni_2N_3SO$	276.42–400.46	21.88 (21.48)	4Cl
$C_{12}H_{11}Ni_2N_3SO$	400.46–		
$[CuL_2Cl_2].2H_2O$			
$C_{24}H_{26}Cl_2CuN_6S_2O_4$	67.21–150.72	5.45 (5.92)	$2H_2O$
$C_{24}H_{22}Cl_2CuN_6S_2O_2$	150.72–334.60	10.73 (10.37)	2Cl
$C_{24}H_{22}CuN_6S_2O_2$	334.60–		
$[FeL_2Cl_2].C_2H_5OH$			
$C_{26}H_{28}Cl_2FeN_6S_2O_3$	50.64–184.46	6.94 (6.66)	C_2H_5OH
$C_{24}H_{22}Cl_2FeN_6S_2O_2$	184.46–334.16	10.10 (10.37)	2Cl
$C_{24}H_{22}FeN_6S_2O_2$	334.16–		

ligand and complexes were calculated within the corresponding temperature ranges.

The ligand (**L**) is stable up to 115.2°C but then decomposes in three steps 115.2–200.4°C, 200.4–300.2°C and 300.2–620.8°C. In the decomposition process of the ligand, the weight losses correspond to the removal of the $-CH_2CH_3$, $-CHO$ and thiadiazole group at the first, second and third stage of decomposition, respectively. The DTA curve of the ligand exhibits three endothermic peaks at 104.4°C, 190.3°C, 217.3°C, and one exothermic peak at 313.6°C. The three stages of the ligand decomposition are irreversible.[25]

$[CoL(H_2O)_4].2Cl.H_2O$ complex a mass loss occur within the temperature range 50.5–190.6°C corresponding to the loss of hydrated water molecule (% experimental weight 3.87; calculated weight 3.70) and at the temperature range 190.6–330.8°C corresponding to a loss of coordinated water molecules (% experimental weight 15.59; calculated weight 14.81). In the temperature range 330.8–370.2°C a mass loss occur corresponding to a losses of Cl ions (% experimental weight 15.25; calculated weight 15.55)[26,27]

The DTA analysis of Co(II) complex also show endothermic peak around 326.1°C. For this complex the endothermic peak in the temperature range 326.1°C is assigned to the desolvation of the coordination water. This assignment was also confirmed by the weight loss obtained by the TGA curve. The three stages of the decomposition of Co(II) complex were irreversible.

The $[Ni_2LCl_4(H_2O)_4].4H_2O$ complex was stable up to 60.0°C and its decomposition started at this temperature. The first step in the temperature range 60.9–100.9°C may account for the loss of water molecules of hydration (% experimental weight 11.85; calculated weight 11.11). The second step of decomposition within the temperature range 100.9–276.4°C corresponds to the loss of coordinated water molecules (% experimental weight 10.37; calculated weight 11.11). In the DTA curve, sharp endothermic peak observed in range 158.2°C for the complex of Ni(II), in conjunction with the mass loss in the TGA curve corresponding to four water molecules, confirm the stoichiometry $[Ni_2LCl_4(H_2O)_4].4H_2O$ for the Ni(II) complex. In the temperature range 276.4–400.5°C a mass loss occured corresponding to a loss of Cl ligands (% experimental weight 21.88; calculated weight 21.48). In the Ni(II) complex, the endothermic peak at 360.4°C is related to the decomposition of Cl ligands.[28,29]

The thermal decomposition of the $[CuL_2Cl_2].2H_2O$ complex started at 67.0°C. The endothermic peak in the 216.2°C temperature range for Cu(II) complex was assigned to the desolvation of the hydrated water (% experimental weight 5.45; calculated weight 5.92). This is followed by broad more or less strong exothermic peaks located at 200.5 and 276.2°C corresponding to decomposition of the Cl ligands (% experimental weight 10.73; calculated weight 10.37).[30]

The decomposition curve of $[FeL_2Cl_2].C_2H_5OH$ began by a step at 50.6–184.5°C displaying 6.66 % weight loss corresponding to the removal of C_2H_5OH. The second weight loss stage at 184.5–334.2°C refers to the removal of Cl ligands[31] (% experimental weight 10.10; calculated weight 10.37). The DTA curve of the Fe(II) complex exhibits endothermic peak at 83.66°C corresponding to the loss of C_2H_5OH and one exothermic peak at 320.1°C corresponding to the loss of Cl ligands.

The finally products during thermal analysis of the ligand and its complexes were not possible to identify because ligand and its complexes undergo could not complete decomposition until 800°C temperature. The continuation of the decompositions indicate that a higher thermal stability of the complexes. Such stability may refer to the presence of one or/two five-membered rings.[32]

Single crystals of the complexes could not be isolated from any solutions, thus no definite structure could be described. However, the analytical, spectrospic and magnetic data enable us to propose the possible structure.

EXPERIMENTAL

Materials and Physical Measurements

All solvents were analytical grade reagents, used as purchased. The metal salts $CoCI_2.6H_2O$, $CuCI_2.2H_2O$, $NiCI_2.6H_2O$ and $FeCI_2.6H_2O$ and starting materials for the ligand were Merck, Aldrich, Fluka and Alfa Aesar products.

Elemental analyses were carried out on a Leco CHNS-O model 932 elemental analyzer. ^{1}H-NMR spectra were recorded using a model Bruker GmbH DPX-300 MHz FT spectrometer. IR spectra were recorded Perkin Elmer Precisely Spectrum One spectrometer on KBr discs in the wavenumber range of 4000–400 cm^{-1}. Electronic spectral studies were conducted on a Shimadzu model UV-1700 Spectrophotometer in the wavelength 1000–200 nm. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $Hg[Co(SCN)_4]$ as a calibrant. Thermal analyzers (TGA and DTA) were carried out in nitrogen atmosphere with a heating rate of 10°C/min. using Shimadzu DTG-60 AH (Shimadzu DSC 60 A) thermal analyzers.

Preparation of Ligand N-(5-Ethyl-1,3,4-Thiadiazole-2-yl)Terephthalaldehyde Imine (L, $C_{12}H_{11}N_3SO$)

2-Amino-5-ethyl-1,3,4-thiadiazole 0.26 g (0.002 mol) in ethanol 20 mL was added to a hot ethanol solution 15 mL of terephthalaldehyde 0.27 g (0.002 mol). The pH was adjusted to ≈5 using glacial acetic acid (3 mL) . The resultant solution was refluxed for 8 h. After cooling, the solution of the Schiff base was stirred for an additional 10 min. and finally poured into a beaker containing 100 mL of water. The new mixture was allowed to stir for 20 min, and the resulting dark yellow solid was collected by filtration, washed several times with water and dried in air for 48 h. The product was recrystallized from ethanol and washed with cold ethanol. Yield: 0.29 g (60%)

Preparation of $[CoL(H_2O)_4].2Cl.H_2O$

A warm methanol solution (20 mL) of ligand 0.74 g (0.003 mol) was added to a magnetically stirred solution of $CoCl_2.6H_2O$ 0.71 g (0.003 mol) in ethanol (10 mL). The mixture was refluxed for 10 h. Then the volume of the obtained solution was reduced to one-half by evaporation and complex was precipitated by the addition of aceton-water (1:1) to give dark red product. The precipitate was filtered, washed with methanol then dried at room temperature. Yield: 0.67 g (% 48).

Preparation of $[Ni_2LCl_4(H_2O)_4].4H_2O$

A quantity of 0.74 g (0.003 mol) of ligand (L) in methanol (20 mL) was added to a solution of 1.43 g (0.006 mol) $NiCl_2.6H_2O$ in methanol-water mixture (1:1), 10 mL. The mixture was left under reflux with continuous stirring for 10 h where upon the solid complex precipitated. The resulting solid was washed with water followed by diethl ether and dried in a room temperature. Yield: 1.05 g (% 54).

Preparation of $[CuL_2Cl_2].2H_2O$

1.49 g (0.006 mol) of ligand (L) was dissolved in 20 mL absolute methanol in a 100 mL round bottom flask. A solution of 0.51 g (0.003 mol) of $CuCl_2.2H_2O$ in 10 mL absolute methanol-water mixture (1:1) was added dropwise in a 10 min. period with continuous stirring at room temperature. The mixture refluxed overnight. Then the volume of the solutions was reduced to about 10 mL and complex were precipitated with aceton-water (1:1) to give pale green product. The precipitate was filtered, washed with methanol then dried at room temperature. Yield: 1.15 g (% 58).

Preparation of $[FeL_2Cl_2]$.EtOH

A warm methanol solution (20 mL) of ligand 1.47 g (0.006 mol) was added to a magnetically stirred solution of $FeCl_2.6H_2O$ 0.70 g (0.003 mol) in ethanol (15 mL). The mixture was refluxed overnight. Then the volume of the obtained solution was reduced to one-half by evaporation. One day later, the colored solid of the complex formed was filtered, the solid washed with ethanol and methanol, and finally dried at room temperature. Yield: 1.09 g (% 55).

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