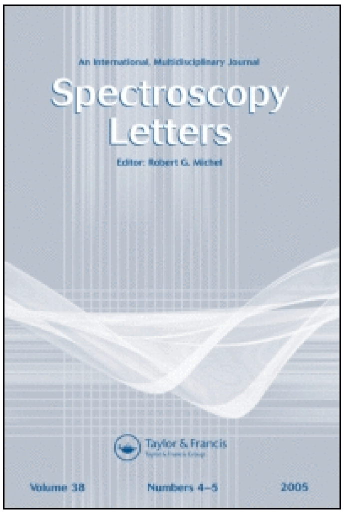

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Synthesis and Spectral Studies of Novel Co(II), Ni(II), Cu(II), Cd(II), and Fe(II) Metal Complexes with N-[5'-Amino-2,2'-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL)

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Synthesis and Spectral Studies of Novel Co(II), Ni(II), Cu(II), Cd(II), and Fe(II) Metal Complexes with N-[5′-Amino-2,2′-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL)

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ABSTRACT Co(II), Ni(II), Cu(II), Cd(II), and Fe(II) complexes with Schiff base derived from 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (**1**) and salicylaldehyde have been prepared. The ligand and its complexes have been characterized by IR, ^{1}H NMR spectra, elemental analyses, magnetic susceptibility, UV-Vis. and thermogravimetry–differential thermal analysis (TGA-DTA). The analytical data show 1:2 metal-to-ligand ratio for Co(II), Ni(II), Cd(II), and Fe(II) and 2:2 metal-to-ligand ratio for Cu(II) complexes. The suggested structures for the *N*-[5′-Amino-2,2′-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL) complexes of Fe(II), Co(II), and Cd(II) are octahedral, for the Ni(II) complex is tetrahedral, and for the Cu(II) complex is square-planar

KEYWORDS 1,3,4-thiadiazole, salicylaldehyde, Schiff base and complexes

INTRODUCTION

The structures and properties of thiadiazole derivatives and related compounds is of great interest owing to their plant growth regulating effects, antimicrobial activity, and industrial applications.[1] In theory, *N,N′*-ligands such as 1,3,4-thiadiazoles are very versatile in that they are able to bridge a wide range of metals[2,3] and can coordinate to many metal ions through nitrogen or sulfur. Transition metal complexes of 1,3,4-thiadiazole derivatives are intriguing from both theoretical and practical viewpoints and are the subject of several industrial applications.[2]

During resent years there have been intense investigations of different classes of thiadiazole compounds many of which are known to possess interesting biological properties such as antimicrobial, antituberculosis, antiinflammatory and analgesic activities.[4,5] Thus, further synthesis and investigation of this group of compounds seems to be well founded.

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In this study, we report the synthesis of Co(II), Ni(II), Cu(II), Cd(II) and Fe(II) complexes of with Schiff base derived from condensation of 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (**1**) and salicylaldehyde. The complexes were formulated on the basis of analytical, spectral and magnetic data. The thermal behaviour of these complexes shows that the hydrated complexes losses water molecules of hydration and etenole molecules in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent step.

EXPERIMENTAL

Materials

Thiosemicarbazide, oxalic acid, phosphorous oxychloride glacial acetic acid, sodium hydroxide and salicylaldehyde were purchased from Merck and used without further purification. All solvents were obtained from Merck or Aldrich. The metal salts $CoCI_2 \cdot 6H_2O$, $CuCI_2 \cdot 2H_2O$, $NiCI_2 \cdot 6H_2O$, $CdCI_2 \cdot H_2O$ and $FeCI_2 \cdot 6H_2O$ were purchased from Merck and were used as received.

Physical Measurements

Elemental analyses (C, H, N, S) were carried out on a Leco CHNS-O model 932 elemental analyzer. ^{1}H NMR spectra were recorded using a Bruker model DPX-300 MHz FT spectrometer. IR spectra were recorded using a Perkin Elmer Precisely Spectrum One spectrometer on KBr disks in the wavenumber range 4000–400 cm^{-1}. Electronic spectral studies were conducted on a Shimadzu model UV-1700 spectrophotometer in the wavelength region 1000–200 nm. Magnetic susceptibilities measurements were performed using the standard Gouy tube technique using $Hg[Co(SCN)_4]$ as a calibrant. Thermal analyses (TGA and DTA) were carried out in nitrogen atmosphere with a heating rate of 15°C/min using Shimadzu TG-60WS AH (Shimadzu DSC 60 A) thermal analyzers.

Synthesis of 2-Amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (1)

A mixture of oxalic acid 5.04 g (56 mmol), thiosemicarbazide 9.48 g (104 mmol), and $POCl_3$ 9.5 mL was warmed at 60°C for 1 h, then the temperature was raised to 95°C for an additional 3 h. The mixture was then poured into the least amount of crushed ice needed, cooled to 15°C, and the pH 10 adjusted to with 10 M NaOH. The resulting cream-coloured precipitate was filtered and washed with DMF, then dried in air.[6]

Synthesis of *N*-[5′-Amino-2,2′-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde Imine (HL)

A solution of 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (**1**); Fig. 1 4.0 g (20 mmol) in 15 mL EtOH was added slowly and dropwise into a solution of salicyaldehyde 2.44 g (20 mmol), and the mixture was stirred at 60°C for 30 min. Five drops of 3 mL glacial acetic acid (AcOH) solution were added to the above-mentioned solution to keep pH 5. The resultant solution was heated on an electromagnetic stirring apparatus to reflux for 3 h. A pale–yellow colored precipitate was filtered and washed with EtOH, then dried in air.

Synthesis of the Metal Complexes

The ligand HL (0.61 g, 2 mmol) was dissolved in 20 mL DMF in a 100-mL round-bottom flask. A solution of 1 mmol metal salt [$CoCl_2 \cdot 6H_2O$ (0.24 g), $NiCl_2 \cdot 6H_2O$ (0.24 g), $CuCl_2 \cdot 2H_2O$ (0.17 g), $CdCl_2 \cdot H_2O$ (0.20 g), and $FeCl_2 \cdot 6H_2O$ (0.41 g) in 10 mL absolute ethanol was added dropwise in a 15-min period with continuous stirring at room temperature. The reaction mixture was then further refluxed for 6 h at 100–120°C. The resulting

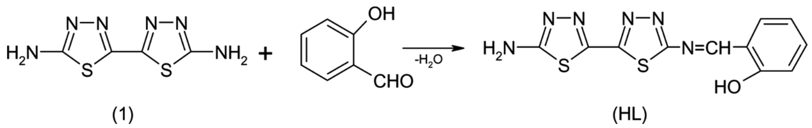


FIGURE 1 Synthesis of the ligand: *N*-[5-amino-2,2-bis(1,3,4-thisdiazole)-5-yl]-2-hydroxybenzaldehyde imine (HL).

precipitates were filtered off and washed with absolute ethanol and DMF, respectively, and were then dried in air.

RESULTS AND DISCUSSION

This study occurred in three stages. In the first stage, the 2-amino-5-(2-amino-1,3,4-thiadiazoleyl)-1,3,4-thiadiazole (**1**) was synthesized by the method described in the literature.[6] In the second stage, the *N*-[5′-amino–2,2′-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxybenzaldehyde imine (HL) was obtained by the reaction of 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1-,3,4-thiadiazole (**1**) and salicylaldehyde. In the last stage, the complex compounds were prepared with the reaction of ligand (HL) and $CoCI_2 \cdot 6H_2O$, $CuCI_2 \cdot 2H_2O$, $NiCI_2 \cdot 6H_2O$, $CdCI_2 \cdot H_2O$, and $FeCI_2 \cdot 6H_2O$ metal salts.

Schiff base and its metal complexes are colored and stable toward air and moisture. The Schiff base is sparingly soluble in hot ethanol, methanol, acetone, and chloroform. However, its metal complexes are generally soluble in DMF and DMSO.

The ligand HL and its new complexes were characterized by elemental analyses and the spectral data that allowed us to assign the coordination mode of ligand HL in these complexes. As seen from data of Table 1, the elemental analyses data of the new complexes were within ±0.4% of the theoretical data calculated for the proposed formulas. The metal-to-ligand ratio of the Co(II), Ni(II), Cd(II), and Fe(II) complexes was found to be 1:2; in addition, there were present ethanol and water. The metal-to-ligand ratio of the Cu(II) complex was found to be 2:2, and the Cu(II) complex has two chloride ions, two molecules of water crystallization, and two DMF. The probable structure of the complexes is shown in Figures 2 and 3.

Infrared Spectra

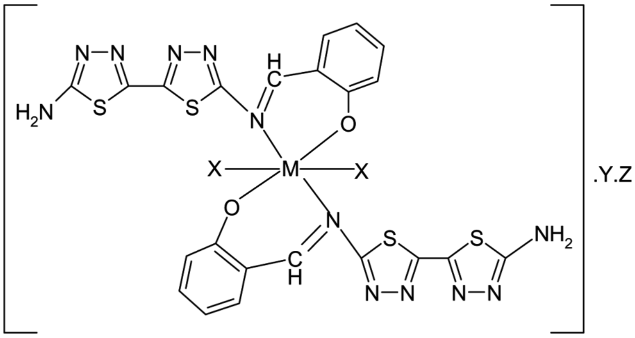
The IR data of the spectra of *N*-[5′-amino–2,2′-bis(1,3,4-thiadiazole)-5-yl]-2-hydroxy benzaldehyde imine (HL) Schiff base and its complexes are listed in Table 2. The IR spectra of the complexes are compared with those of the free ligand in order to determine the coordination sites that may be involved in chelation. There are some guide peaks in the spectra of the ligand, which are of good help for achieving this goal. The position and/or the intensities of these peaks are expected to be changed upon chelation.

In the IR spectrum of 2-amino-5-(2-amino-1,3,4-thiadiazolyl)-1,3,4-thiadiazole (**1**), the characteristic peaks are at 3340 and 3280 cm^{-1} $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$, 1628 $cm^{-1}$$\nu(C{=}N)$ in thiadiazole, and 1514 cm^{-1} $\delta(NH)$, respectively.[6]

TABLE 1 **The Colors, Formula, Formula Weight (FW), Yields, Melting Points (M.P.), Magnetic Moments, and Elemental Analysis Results of the Ligand (HL) and the Complexes**

					Elemental analyses/(%) calculated (found)			
Compounds	FW, (g/mol)	M.P. (°C)	Yield (%)	μ_{eff}(B.M.)[a]	C	H	N	S
Ligand (HL)	304.00	330	66	—	43.42	2.63	27.63	21.05
$C_{11}H_8N_6S_2O$					(43.31)	(2.44)	(26.49)	(21.02)
(Pale yellow)								
$[CoL_2(C_2H_5OH)_2] \cdot 4C_2H_5OH$	940.93	336	50	3.30	43.36	5.30	17.85	13.60
(Dark green)					(43.06)	(5.14)	(17.79)	(13.35)
$C_{34}H_{50}N_{12}S_4O_8Co$								
$[NiL_2] \cdot 2H_2O \cdot 3C_2H_5OH$	838.71	>360	62	2.35	40.06	4.29	20.03	15.26
(Dark red)					(40.15)	(3.94)	(19.73)	(15.16)
$C_{28}H_{36}N_{12}S_4O_7Ni$								
$[Cu_2L_2] \cdot 2Cl.2H_2O \cdot 2DMF$	986.00	335	65	0.92	34.08	3.25	19.88	12.98
(Pale green)					(34.01)	(3.15)	(19.69)	(12.86)
$C_{28}H_{32}N_{14}S_4O_6Cu_2Cl_2$								
$[FeL_2(H_2O)_2] \cdot 2H_2O \cdot 3C_2H_5OH$	871.85	345	54	4.92	38.50	4.59	19.27	14.68
(Dark red) $C_{28}H_{40}N_{12}S_4O_9Fe$					(38.21)	(4.20)	(18.98)	(14.41)
$[CdL_2(C_2H_5OH)_2] \cdot 4H_2O \cdot C_2H_5OH$	928.41	340	60	Dia	36.19	4.31	18.10	13.79
(Gray) $C_{28}H_{40}N_{12}S_4O_9Cd$					(36.33)	(4.24)	(18.05)	(13.46)

[a] Magnetic moment at 30°C, B.M.: Bohr Magneton.



M =	Co(II)	Ni(II)	Cd(II)	Fe(II)
X	$2C_2H_5OH$	_	$2C_2H_5OH$	$2H_2O$
Y	$4C_2H_5OH$	$3C_2H_5OH$	C_2H_5OH	$2H_2O$
Z	_	$2H_2O$	$4H_2O$	$3C_2H_5OH$

FIGURE 2 **Suggested structure of the octahedral Co(II), Co(II), Fe(II), and tetrahedral Ni(II) complexes of the ligand (HL).**

In the IR spectra of the ligand HL, the most characteristic bands are at 3379 cm^{-1} ν(OH) and 1679 cm^{-1} azomethine ν(HC=N) and 3284 cm^{-1} $\nu_s(NH_2)$. The IR spectra of the Schiff base showed the absence of band at 1730 cm^{-1} due to carbonyl ν(C = O) stretching vibration (present in the starting material) and the appearance of a strong new band at 1679 cm^{-1} assigned as azomethine ν(HC=N) vibration.[7,8]

The infrared spectra of the ligand containing OH group show a strong band at 3379 cm^{-1} due to ν(OH). However, The IR spectra of the dehydrated complexes indicated the disappearance of the OH bands from the spectra of the complexes by displacement of all phenolic protons by metal ions. The IR spectrum for intensity of the OH bands indicates partial removal of protons from the OH groups.[9]

The spectra of all the complexes exhibited intense broad bands at 3615–3392cm^{-1} due to ν(OH) of H_2O.[8] The presence of lattice and coordinated water or ethanol molecules is also confirmed by thermogravimetric analyses.[7]

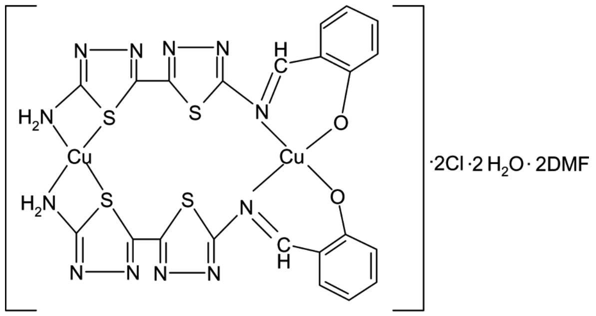


FIGURE 3 **Suggested structure of the square-plant Co(II) complex of the lignad (HL).**

Phenolic ν(C–O) stretching vibration band is observed at 1302 cm^{-1} in the free ligand. In all complexes, this band appears at lower frequencys in the 1297–1253 cm^{-1} region, confirming the involvement of the phenolic group in complex formation.[10]

In the Schiff base ligand, the strong band observed at 1684 cm^{-1} can be assigned to the ν(C=N) azomethine stretching vibration. On complexation, this band was shifted to lower frequency of the azomethine nitrogen atom to the central metal ion.[10]

The spectra of the complexes show a few new absorption bands in the 480–465 cm^{-1} and 587–510 cm^{-1} ranges, assigned to ν(M–N) and ν(M–O), respectively. From the IR results, it may be concluded that the Schiff base ligand is bidentate and coordinates with the metal ion through the phenolic oxygen and azomethine nitrogen atoms.[11,12]

Other characteristic IR bands observed in the spectra of the Schiff bases at 1492–1430, 1060–948, and 758–754 cm^{-1} have been assigned to the ν(>C=N–N=C<) ν(N–N), and ν(C–S–C) modes of vibrations, respectively, of the thiadiazole ring. In the spectra of the Co(II), Ni(II), Cd(II), and Fe(II) complexes, the ν(>C=N–N=C<) (cyclic), ν(N–N), and ν(C–S–C) vibrations remain almost unchanged, indicating thereby noninvolvement of the ring nitrogen and sulfur in the coordination.[7]

The IR spectrum of the ligand exhibits a NH_2 peak at 3280 cm^{-1}. The position of this band remains almost unaffected showing only minor shifts to lower frequency in the spectra of Co(II), Ni(II), Cd(II), and Fe(II) complexes, indicating thereby the noninvolvement of the NH_2 group in the process of coordination.[13]

In the Fe(II) complex, the IR bands at 894–769 cm^{-1} $\nu(H_2O)$ of coordinated water are an indication of the binding of the water molecules to the metal ions. New bands are found in the spectra of the complex in the 587–510 cm^{-1} region, which are assigned to ν(M–O) stretching vibrations.[14]

The $\nu(NH_2)$ and ν(C–S–C) bands of the free ligand are shifted considerably to lower wavenumbers (Table 2) supporting coordination of the ligand to the Cu(II) ion via the amino nitrogen atom.[15] The IR and spectroscopic data, therefore, suggest that the ligand is coordinated to the Cu(II) ion via the

TABLE 2 **Characteristic IR Bands (cm^{-1}) of the Ligand HL and Its Complexes in KBr Pellets**

Assignment	Ligand	Co(II)	Ni(II)	Cu(II)	Fe(II)	Cd(II)
ν(O–H)	3379	3406	3401	3392	3399	3392–3410
$\nu(NH_2)$	3287	3285	3290	3266	3286	3277
Aromatic ν(C–H)	3119	3153	3159	3054–3150	3173	3173
(CH = N) Azomethine	1684	1653	1679	1653	1650	1654
ν(arom.,C = C)	1610	1602	1604	1600	1608	1608
δ(NH) (in plane)	1570	—	—	1527	1572	—
ν(>C = N–N = C<) in Thiadiazole	1492	1439–1499	1430–1489	1426–1490	1430–1489	1434–1494
ν(C–O)	1302	1284	1295	1297	1271	1253
ν(N–N) in Thiadiazole	1060–948	943–1056	949–1054	949–1056	950–1060	951–1061
ν(C–S–C) in Thiadiazole	758–754	754	754	723	753	756
ν(M–O)	—	570	510	587	574	577
ν(M–N)	—	480	474	469	467	465

amino nitrogen and the thiadiazole sulfur atom.[16] A characteristic band due to Cu–S stretching is expected to appear in the IR 330–300 cm^{-1} region.[17]. In the IR spectrum of the complexes, Cu–S bands would not be observed in the 4000–400 cm^{-1} range.

The IR spectrum of the Cu(II) complex shows a strong band at 1650 cm^{-1} assigned to a ν(C = O) vibration of the DMF molecules.[18]

In the Cu(II) complex, the chloride ions do not coordinate with the metal ions, as in the CI^- test with $AgNO_3$, white AgCI salt precipated.

^{1}H NMR Spectra

The ^{1}H NMR spectrum of the Schiff base was recorded in dimethylsulfoxide (DMSO-d_6) solution using tetramethylsilane (TMS) as internal standard. The ^{1}H NMR spectra of the Schiff base (HL), its diamagnetic Cd(II) complex, and the chemical shifts of the different types of protons are listed in Table 3. The Schiff base exhibited signals due to all the expected protons in their expected region. These were compared with the reported signals of known structurally related compounds and give further support for the composition of Schiff base as well as its complex suggested by their IR and elemental analyses data. Comparison of the chemical shifts of the uncomplexed Schiff base shows the resonances are shifted upon complexation. Upon examination, it was found that the phenolic-OH signal, appearing in the spectrum of ligand (HL) at 11.20 ppm, is completely dissappeared in the spectra of its Cd(II) complex indicating that the OH proton is removed by the chelation with Cd(II) ion. The signal observed at 3.40 and 1.10 ppm with an integration corresponding with protons in case of Cd(II) complex are assigned to CH_2 and CH_3 group, respectively. The presence of coordinated water molecules in the Cd(II) complex is confirmed by the presence of a new signal at around 3.75 ppm.[12] The singlet at 9.00 ppm was attributed to the proton of the azomethine group. This proton undergoes downfield shift in the Cd(II) complex indicating participation of this group in coordination of the metal ion. In the spectra of Schiff base, the phenyl proton multiplet was observed between 8.50 and 6.50 ppm. A broad peak at 8.40 ppm was attributed to the NH_2 proton, which disappeared on the addition of D_2O due to the proton exchange.[19] Because the other complexes are paramagnetic, their ^{1}H NMR spectra could not be obtained.

TABLE 3 **^{1}H NMR Spectral Data of the Ligand HL and Its Diamagnetic Cd(II) Complex Recorded in DMSO-d_6 Solution**

Compound	^{1}H NMR signals (δ, ppm) and their assignments
Ligand (HL)	11.20 (s, 1H, Ar-OH), 9.00 (s, 1H, CH=N), 6.50–8.50 (m, 4H, Ar-CH), 8.40 (2H, NH_2)
$[CdL_2(C_2H_5OH)_2]\cdot 4H_2O\cdot C_2H_5OH$	9.15 (s, 1H, CH=N), 6.55–8.58 (m, 4H, Ar-CH), 8.43 (2H, NH_2), 4.78 (3H, 0H), 3.75 (broad, 8H, H_2O), 3.40 (q, 4H, CH_2), 3.20 (m, 2H, CH_2), 1.10 (t, 6H, CH_3), 0.90 (m, 3H, CH_3)

Magnetic Susceptibility and Electronic Spectra Measurements

The UV-Vis spectra of the ligand and the complexes were recorded in the DMF solution in the

TABLE 4 **Electronic Spectral Data of the Ligand HL and Its Complexes (nm) (in DMF)**

Compounds	Wavelength in nm (ε)			
Ligand (HL)	260, 318–377 (1125, 160) $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	—	—	—
$[FeL_2(H_2O)_2]\cdot 2H_2O\cdot 3C_2H_5OH$	303–330 (150) $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	424 (165) $L \rightarrow M$	670 (14) $^5T_{2g} \rightarrow {}^5E_g$	
$[CoL_2(C_2H_5OH)_2]\cdot 4C_2H_5OH$	301 (130) $\pi \rightarrow \pi^*$	479–500 (62) $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	703–710 (22) $^4T_{1g}(F) \rightarrow {}^4A_{2g}$	
$[NiL_2]\cdot 2H_2O\cdot 3C_2H_5OH$	328–354 (3000, 2080) $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	433–477 (560, 520) $L \rightarrow M$	600 (240) $^3T_1(F) \rightarrow {}^3T_1(P)$	
$[Cu_2L_2]\cdot 2Cl\cdot 2H_2O\cdot 2DMF$	303–350 (120) $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	433 (55) $L \rightarrow M$	450 (46) $^2B_1 \rightarrow {}^2E$	641 (25) $^2B_1 \rightarrow {}^2A_1$
$[CdL_2(C_2H_5OH)_2]\cdot 4H_2O\cdot C_2H_5OH$	265 (1120) $\pi \rightarrow \pi^*$	307–360 (1450, 1250) $L \rightarrow M$		

ε =molar extinction coefficient (L mol^{-1} cm^{-1}).

wavelength range 200–800 nm. The corresponding magnetic susceptibility and electronic spectra measurements are collected in Tables 1 and 4.

The band appearing in the range 218–318 nm is attributed to $\pi \rightarrow \pi^*$ transition of the benzene ring of the ligand. This band is red shifted to 265–328 nm. The other bands observed in the region 318–377 nm in the free ligand are reasonably accounted for by $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions for the phenolic-OH and azomethine moieties, respectively. In the complexes, these bands are shifted to longer wavelength as a consequence of coordination to the metal, comfirming the formation of Schiff base metal complexes.[20,21] The spectra of the complexes further display a band in the range 424–500 nm, which might be assigned to charge transfer transition from the ligand to metal ions (L → M).[13]

The magnetic moment value (3.30 B.M.) for the $[Co(L)_2(C_2H_5OH)_2]\cdot 4C_2H_5OH$ complex is near the only spin value for high-spin octahedral complexes. The electronic spectrum shows two bands at 479–500 nm and 703–710 nm attributed to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively, in an octahedral geometry around the Co(II) ion. The band observed at 436 nm is assigned to Co(II) → L charge transfer.[8,22]

The band in the region 600 nm attributable to $^3T_1(F) \rightarrow {}^3T_1(P)$ transition is consistent with a tetrahedral geometry around the Ni(II) ion. The low-energy band expected for the $^3T_1(F) \rightarrow {}^3A_2(F)$ transition in tetrahedral Ni(II) complex is observed in the region 400 nm. An intense absorption band in the 433–477 nm region may be due to a charge transfer process.[10,23]

The electronic spectrum of the Cu(II) complex shows an absorption band at 433 nm attributed to the S → Cu(II) transition. Square-planar geometry is suggested for Cu(II) complex from the presence of bands at 641 and 450 nm. The first band is assigned to the $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2A_1$ transitions, while the second band is due to charge transfer. The magnetic moment value for Cu(II) complex is normal and lower (0.92 B.M.) than expected (1.73 B.M.) for unpaired electron. The lower value may be due to strong interaction with the neighboring molecule.[8,24]

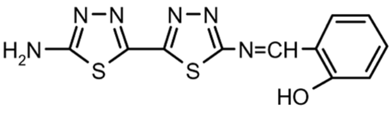
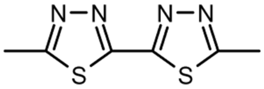
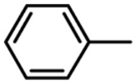
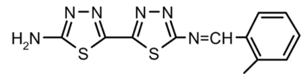
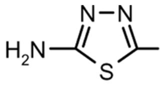
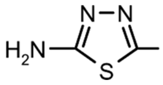
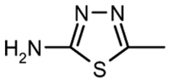
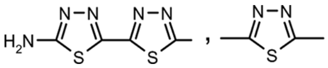
The Fe(II) complex has a magnetic moment value of 4.92 B.M., which is consistent with two high spin octahedral geometry. The diffuse reflectance spectrum shows two absorption bands at 670 nm and 460 nm, which are assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition and charge transfer, respectively. Therefore, the magnetic moment value and position of the bands confirm the octahedral geometry.[25]

The complex of Cd(II) is diamagnetic. In analogy with those described for Cd(II) complexes containing N–O donor Schiff base and according to the empirical formulae of this complex, we proposed an octahedral geometry for this complex.[12]

Thermal Studies

The thermal stability of the complexes and ligand was investigated by a combination of TGA and DTA. The TGA and DTA curves were obtained at a heating rate of 15°C/min in a nitrogen atmosphere over the temperature range of 25.0–900.0°C. The thermal data are summarized in Table 5. The results obtained are in good agreement with the theoretical formula suggested from the elemental analyses. The weight losses for ligand and complexes were calculated within the corresponding temperature ranges.

TABLE 5 **Proposed Decomposition Steps and the Respective Mass Losses of Ligand HL–Metal Complexes**

Equations	Temperature (°C)	% Loss in weight % Found (% calculated)	Decomposition products
	50.37–333.56	10.85 (11.11)	OH, NH_2
$C_{11}H_8N_6S_2O$ [HL]			
$C_{11}H_5N_5S_2$	333.56–470.18	55.56 (55.55)	
C_7H_5N	470.18–645.25	25.33 (25.18)	
CHN	645.25–700.10	8.88 (7.41)	N = CH
$[CoL_2(C_2H_5OH)_2]\cdot 4C_2H_5OH$ $(C_{34}H_{50}N_{12}S_4O_8Co)$	50.16–380.10	29.33 (29.68)	$6C_2H_5OH$, $1/2O_2$
		1.70 (1.35)	
$C_{22}H_{14}N_{12}S_4O_2Co$	380.10–845.24	61.00 (60.00)	2 
CoO	845.24	7.96 (8.15)	CoO
$[NiL_2].2H_2O\cdot 3C_2H_5OH$ $C_{28}H_{36}N_{12}S_4O_7Ni$	25.85–280.48	4.29 (4.44)	$2H_2O$, $3C_2H_5OH$
		16.45 (15.56)	
$C_{22}H_{14}N_{12}S_4O_2Ni$	280.48–463.58	23.85 (23.70)	2 
$C_{18}H_{10}N_9S_3O_2Ni$	463.58–900.00		
$[Cu_2L_2]\cdot 2Cl\cdot 2H_2O\cdot 2DMF$ $C_{28}H_{32}N_{14}S_4O_6Cu_2Cl_2$	70.34–160.81	3.65 (3.70)	$2H_2O$
$C_{28}H_{28}N_{14}S_4O_4Cu_2Cl_2$	160.81–340.12	14.81 (14.81)	2Cl, 2DMF
$C_{22}H_{14}N_{12}S_4O_2Cu_2$	340.12–900.00		
$[FeL_2(H_2O)_2]\cdot 2H_2O\cdot 3C_2H_5OH$ $C_{28}H_{40}N_{12}S_4O_9Fe$	50.35–180.63	4.13 (3.70)	$2H_2O$
$C_{28}H_{36}N_{12}S_4O_7Fe$	180.63–330.42	19.96 (19.26)	$2H_2O$, $3C_2H_5OH$
$C_{22}H_{14}N_{12}S_4O_2Fe$	330.42–489.16	22.94 (22.22)	2 
$C_{18}H_{10}N_6S_2O_2Fe$	489.16–900.00		
$[CdL_2(C_2H_5OH)_2]\cdot 4H_2O\cdot C_2H_5OH$ $C_{28}H_{40}N_{12}S_4O_9Cd$	80.32–184.75	7.76 (7.41)	$4H_2O$
$C_{28}H_{32}N_{12}S_4O_5Cd$	184.75–284.18	14.86 (14.82)	$3C_2H_5OH$
$C_{22}H_{14}N_{12}S_4O_2Cd$	284.18–450.72	10.77 (9.63)	
$C_{20}H_{10}N_9S_3O_2Cd$	450.72–770.16	28.87 (29.63)	
$C_{14}H_8N_2O_2Cd$	770.16–900.00		

The ligand is stable up to 50.37°C, and its decomposition started at this temperature. The ligand shows five-step weight loss. The loss of the OH and NH_2 groups and simultaneously in the first and second steps between 50.37°C and 333.56°C with one endothermic DTA peak at 83.35°C and violently one exothermic peak at DTA 219.48°C. The 30 steps in the 333.56–470.18°C range corresponds with the exothermic elimination of the second thiadiazole rings. The experimental mass loss of 55.55% agrees well with the calculated mass loss of 55.56%. The 40 steps in the 470.18–645.25°C range corresponds with the exothermic elimination of the benzene ring. The experimental mass loss of 25.18% agrees well with the calculated mass loss of 25.33%. The final step in the 645.25–700.10°C step shows elimination of one of the CH = N groups. The experimental mass loss of 7.41% agress well with the calculated mass loss of 8.88%.[21,26]

The DTA curve of the ligand shows an endothermic process around 333°C that corresponds with the rupture of coordinated band and simultaneous melting of the ligand.[27]

The decomposition curve of $CoL_2(C_2H_5OH)_2] \cdot 4C_2H_5OH$ begins by a step at 50.16–380.10°C displaying 29.68% weight loss corresponding with the removal of $6C_2H_5OH$ (calcd. mass loss 29.33%) and $1/2O_2$ 1.35% (calcd. mass loss 1.70%). The second weight loss stage at 380.10–845.24°C refers to the removal of the fully organic part of the ligand decomposition. The decomposition steps for the complex end with CoO as a final product with a weight loss of 7.96% (calcd. mass loss 8.15%). The DTA curve of the Co(II) complex shows endothermic peaks at 80.34°C and 215.27°C corresponding with the loss of $6C_2H_5OH$ (29.68%) and $1/2O_2$ (1.35%) and two exothermic peaks at 495.20°C and 525.18°C corresponding with the second weight loss.[8,28]

The thermogram of $[NiL_2] \cdot 2H_2O \cdot 3C_2H_5OH$ complex shows decomposition steps within the temperature range 25.85–463.58°C. The first decomposition step with an estimated mass loss of 4.29% (calcd. mass loss 4.44%) and 16.45% (calcd. mass loss 15.56%), within the temperature range 25.85–280.48°C, may be attributed to the liberation of water molecules of hydration and $3C_2H_5OH$.[29] The IR spectra of the complexes are characterized by the appearance of a broad band in the region 3401 cm^{-1} due to the ν(O–H) frequency of water of hydration and ethanol. The water and ethanol content was also identified by the elemental analyses.[21,30] In the decomposition process of the Ni(II) complex, the mass losses corresponded with two 2-amino-1,3,4-thiadiazole groups leaving in the second stage of the decomposition 23.85% (calcd. mass loss 23.70%). The DTA curve of the Ni(II) complex shows endothermic peak at 275.34°C corresponding with the loss of molecules of hydration water and one exothermic peak at 400.16°C.[12]

The curve for $[Cu_2L_2] \cdot 2Cl_2 \cdot 2H_2O \cdot 2DMF$ showed stability to 70.00°C, above which a weight loss by 3.65% (calcd. mass loss 3.70%) corresponds with removal of two hydration water molecules. The second stage ending at 160.81–340.12°C is assigned to the elimination of 2Cl and 2DMF groups from the ligand accompanied by a weight loss of 14.81% (calcd. mass loss 14.81%).[31,32] The DTA curve of the Cu(II) complex shows one endothermic peak at 110.35°C corresponding with the loss of hydrated water molecules and one exothermic peak at 280.50°C.[33,34] The exothermic peak is likely due to the remove of 2Cl and 2DMF.

The thermogram of $[FeL_2 \cdot H_2O)_2] \cdot 2H_2O \cdot 3C_2H_5OH$ complex shows decompositions steps within the temperature range 50.0–500.0°C. The first (50.35–180.63°C) is due to removal of the two hydration water molecules with a weight loss of 4.13% (calcd. mass loss 3.70%). The second (180.63–330.42°C) with 19.96% (calcd. mass loss 19.26%) weight loss is associated with the removal of two coordinated waters as well as $3C_2H_5OH$. The third (330.42–489.16°C) with 22.94% (calcd. mass loss 22.22%) confirms elimination of the two 2-amino-1,3,4-thiadiazole molecules.[21] The DTA curve of the Fe(II) complex shows one endothermic peak at 230.35°C and two exothermic peaks at 260.55°C and 350.40°C. The first one is related to removal of the hydration water molecules, whereas the others are the second and third steps of decomposition.[28]

The thermogram of $[CdL_2(C_2H_5OH)_2] \cdot 4H_2O \cdot C_2H_5OH$ complex shows decomposition steps within the temperature range 80.0–500.0°C. The first two steps of decomposition within the temperature range 80.32–284.18°C correspond with the loss of water molecules of hydration and $3C_2H_5OH$ molecules with a mass loss of 7.76% (calcd. mass loss 7.41%)

and 14.86% (calcd. mass loss 14.82%), respectively.[22,12] The subsequent steps correspond with the removal of the organic part of the ligand. The DTA curve of the Cd(II) complex shows two endothermic peak at 180.34°C and 250.34°C. The endothermic peaks are likely due to the loss of molecules of hydration water and $3C_2H_5OH$ molecules.[22]

The weight losses for Co(II), Ni(II), Cu(II), Fe(II), and Cd(II) complexes were found to be approximately the same, when expressed as the percentages calculated stoichiometrically from their chemical formulas given in Table 5.

The final products formed during thermal analysis of the ligand and its complexes were not possible to determine because the ligand and its complexes of the decompositions could not complete until 900°C temperature, except for the Co(II) complex. The continuation of the decompositions indicates a higher thermal stability of the complexes. Such stability may refer to the presence of one or/two five-membered rings.[24]

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

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