Chapter 17
Synthesis and Characterization of Co(II), Ni(II) and Cu(II) Complexes with Thio-1,3,4-oxadiazole Derivatives

Hikmat Ali Mohamad and Beriwan Mohamad Hamad Ameem

Abstract Transition metal complexes of Ni(II), Co(II) and Cu(II) with the ligands [$\mathbf{L_1}$ = 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)benzenamine, $\mathbf{L_2}$ = (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenylimino)indolin-2-one, $\mathbf{L_3}$ = 2,2′-(5,5′-1,4-phenylene)bis(1,3,4-oxadiazole-5,2-diyl)bis(sulfanediyl)dibenzenamine], derived from the condensation of 5-phenyl-1,3,4-oxadiazole-2-thiol, 5,5′-(1,4-phenylene)bis(1,3,4-oxadiazole-2-thiol) and 2-aminothiophenol or isatin were synthesized. The ligands and their complexes were characterized on the basis of analytical, conductance, magnetic data, infrared, electronic spectra and ^{1}H-NMR data. IR spectral data suggest that the ligands were chelated with the ionic metal through S and N atoms. On the basis of the spectral, physicochemical data as well as magnetic moment measurements, octahedral geometries were assigned for the complexes.

Keywords Isatin · 2-aminothiophenol · 1,3,4-oxadiazole-2-thiol · Nuclear magnetic resonance · Infrared

17.1 Introduction

Oxadiazoles are five membered, aromatic heterocycles that contain three hetero atoms on the same ring [1]. There are four isomers of oxadiazoles (Fig. 17.1) of which 1,3,4-oxadiazole has enormous importance [2]. 1,3,4-Oxadiazole is considered to be derived from furan by replacement of two –CH= groups by two pyridine type nitrogen –N=, and is a cyclic compound containing one oxygen and two nitrogen atoms in a five-membered ring [3].

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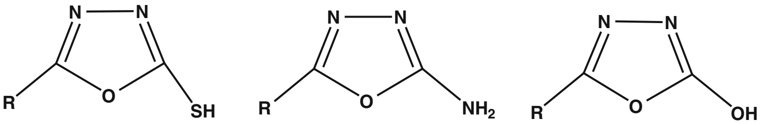
1,2,4-oxadiazole **1,2,3-oxadiazole** **1,3,4-oxadiazole** **1,2,5-oxadiazole**

Fig. 17.1 Isomers of oxadiazole



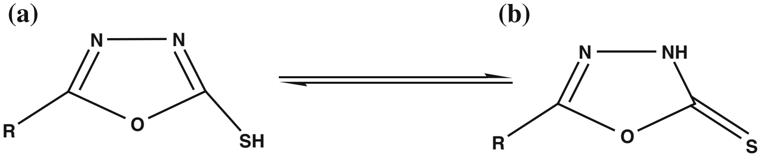
[I] [II] [III]

Fig. 17.2 Derivatives of 1,3,4-oxadiazole

Three main derivatives of 1,3,4-oxadiazole were prepared, namely **I**, **II**, **III**, and from these three derivatives a large number of compounds were prepared depending upon the nature and the type of the substitutions at the position 2 and 5 (Fig. 17.2).

Attention has been concentrated on **[I]** due to the biological activity of the thiol group, and the ligand ability to form complexes with many transition metal ions. Derivative **[I]** can exist in two tautomeric forms **[Ia]** and **[Ib]**, the shift to any one form being induced by reaction conditions [4] (Fig. 17.3).

There are several methods for the synthesis of 1,3,4-oxadiazole, most of them being multisteps and generally involving cyclization of acid hydrazides with a variety of anhydrous reagents such as thionyl chloride, phosphorous oxychloride and sulfuric acid, usually under hard reaction conditions [5]. Recently some efficient techniques have been reported for the synthesis of 1,3.4-oxadiazoles, especially from readily available carboxylic acids and acid hydrazides [5]. 1,3,4-Oxadiazoles, especially 2,5-disubstituted-1,3,4-oxadiazole derivatives, have a broad spectrum of biological activity in both the agrochemicals and pharmaceutical field, such as insecticidal, herbicidal, antibacterial, antifungal, analgesic, antiinflammatory, antimalarial, antiviral, anti-HBV, anticancer, anti-HIV, antitubercular and anticonvulsant [6]. The reason behind all these mentioned activities of



Thiol **[I]** **Thione**

Fig. 17.3 Tautomeric forms of **[I]**

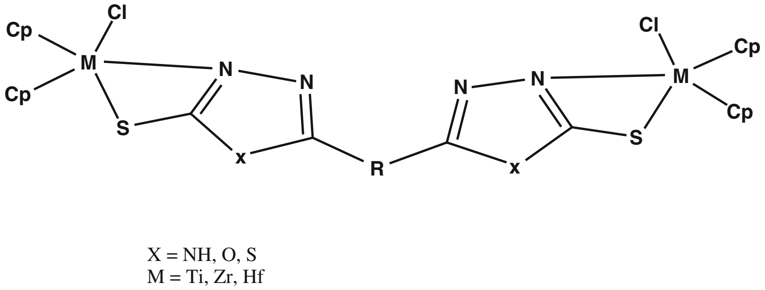


Fig. 17.4 Structures of binuclear complexes of [{(η^5-C_5H_5)$_2$M}$_2$$Cl_2$(L)]

oxadiazoles is their metabolic profile and their ability to engage in hydrogen bonding [7]. The 1,3,4-oxadiazole-2-thiones represent an important type of compounds in the field of coordination chemistry because of their potential multifunctional donor sites, namely, either exocyclic sulphur or endocyclic nitrogen [8]. Since 1,3,4-oxadiazole-2-thiones are biologically active compounds, information about their 3-dimensional structures may be of great interest for rational drug design. 1,3,4-Oxadiazole-2-thione consists of an equilibrium mixture of its thione and thiol forms, and therefore it will be of interest to investigate the mode of coordination of oxadiazole in their complexes [9]. Binuclear complexes of [{(η^5-C_5H_5)$_2$M}$_2$$Cl_2$(L)] ($M$ = Ti, Zr or Hf) (Fig. 17.4) were prepared in dry tetrahydrofuran in the presence of *n*-butylamine and were characterized by magnetic moment and spectral data (UV-Vis, IR, ^{1}H-NMR and ^{13}C-NMR) [10].

In this article, the preparation and characterization of new ligands [$\mathbf{L_1}$ = 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)benzenamine, $\mathbf{L_2}$ = (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenylimino)indolin-2-one and $\mathbf{L_3}$ = 2,2′-(5,5′-1,4-phenylene) bis(1,3,4-oxadiazole-5,2-diyl)bis(sulfanediyl)dibenzenamine] and their complexes with Ni(II), Co(II) and Cu(II) are presented.

17.2 Materials and Methods

All chemicals were of analytical reagent grade and purchased from Fluka, Merck, Alpha or BDH and were used as supplied. Conductivity measurements of 10^{-3} M solution of the complexes in DMSO were carried out with a Jenway conductivity meter 4200. Infrared spectra were recorded on a Shimadzu FT-IR 8400 spectrometer in the 200–4000 cm^{-1} range. The UV/Vis spectra were recorded on a spectrophotometer AE-UV 1609 in DMSO solvent. Melting points were measured using a melting point-MPD-100 Pixel Technology Co. Ltd. Magnetic susceptibility was measured on a Bruker magnet BM6 at 25 °C. ^{1}H-NMR spectra of ligands were carried out on a Bruker ultra shield 300 MHz with TMS as internal reference, in Al-ALBayt University Central Labs (Jordan), in deuterated DMSO as solvent.

17.2.1 Synthesis of Ligands

17.2.1.1 Synthesis of L_1, 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) benzenamine

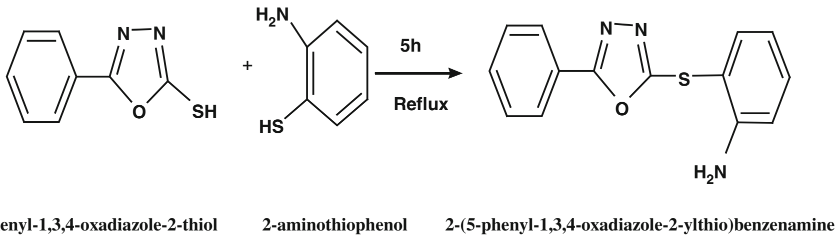
A solution of 2-aminothiophenol (0.375 g, 0.3 ml, 3 mmol) was added to a solution of 5-phenyl-1,3,4-oxadiazole-2-thiol (0.534 g, 3 mmol) in 50 ml of ethanol. The mixture was refluxed for 5 h (Scheme 17.1). The reaction mixture was poured into ice water. The resulting light green precipitate was filtered off, dried and recrystallized from methanol.

17.2.1.2 Synthesis of L_2, (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio) phenylimino)indolin-2-one

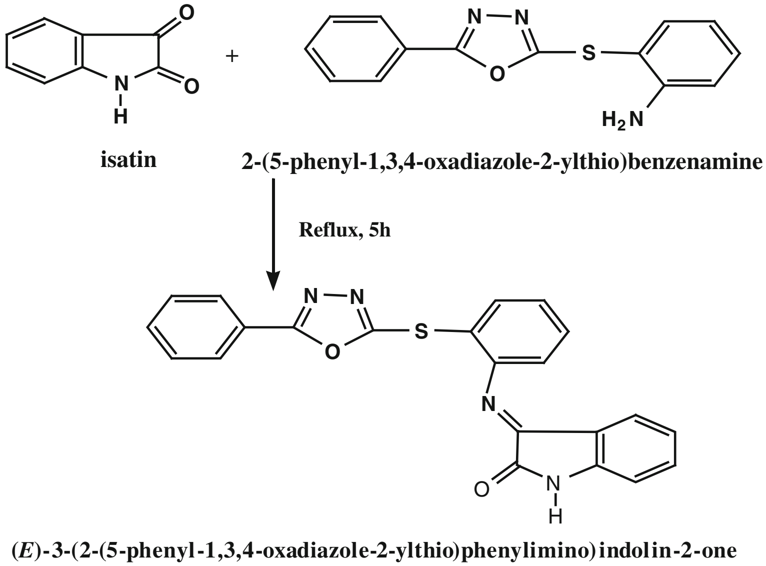
A solution of $\mathbf{L_1}$ (0.807 g, 4 mmol) in 20 ml of ethanol was added to an isatin solution (0.58 g, 4 mmol) dissolved in 10 ml of ethanol. Two drops of glacial acetic acid were added and the mixture was then refluxed for 5 h (Scheme 17.2). The reaction mixture was poured into ice water to give an orange precipitate. The precipitate was filtered off, washed with diethyl ether, dried and recrystallized from ethanol (Scheme 17.2).

17.2.1.3 Synthesis of L_3, 2,2′-(5,5′-1,4-phenylene)bis (1,3,4-oxadiazole-5,2-diyl)bis(sulfanediyl)dibenzenamine

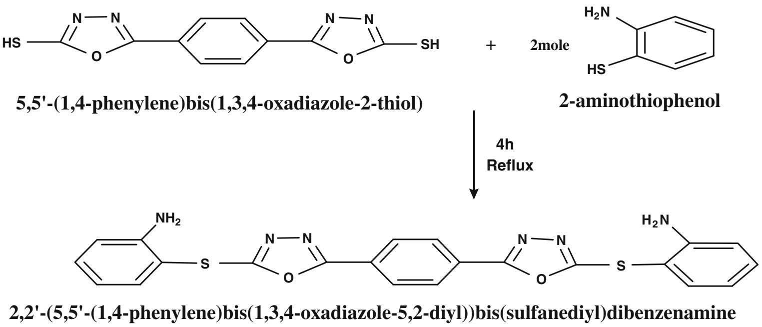
A solution of 2-aminothiophenol (0.5 g, 0.4 ml, 4 mmol) was added to a solution of 5,5′-(1,4-phenylene)bis(1,3,4-oxadiazole-2-thiol) (0.55 g, 2 mmol) in 30 ml of ethanol. The mixture was refluxed for 4 h, then poured into ice water to give a light green precipitate. The precipitate was filtered off, dried and recrystallized from ethanol (Scheme 17.3).



Scheme 17.1 Synthesis of $\mathbf{L_1}$



Scheme 17.2 Synthesis of $\mathbf{L_2}$



Scheme 17.3 Synthesis of $\mathbf{L_3}$

17.2.2 Synthesis of Metal Complexes

17.2.2.1 Synthesis of $[Ni(L_1)_2Cl_2]$

A clear solution of ligand $\mathbf{L_1}$, 2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)benzenamine (0.538 g, 2 mmol) in 10 ml of absolute ethanol was added to a solution of $NiCl_2.6H_2O$ (0.237 g, 1 mmol) in 10 ml of ethanol. The reaction mixture was refluxed for 2 h until a green precipitate was formed. The precipitate was filtered off and washed several times with diethyl ether.

17.2.2.2 Synthesis of $[M(L_2)Cl_2(H_2O)_2]$

A solution of $NiCl_2.6H_2O$ or $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$ (0.33 mmol) in 10 ml of ethanol was added to 10 ml ethanolic solution of (E)-3-(2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)phenylimino)indolin-2-one (**L$_2$**) (0.133 g, 0.33 mmol). The reaction mixture was refluxed for 2 h, then the mixture was left for 24 h to give a precipitate which was filtered off, washed with ethanol and diethyl ether.

17.2.2.3 Synthesis of $[M_2(L_3)Cl_4(H_2O)_4]$

A solution of $NiCl_2.6H_2O$ or $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$ (1 mmol) in 10 ml of ethanol was added to 10 ml ethanolic solution of [2,2′-(5,5′-1,4-phenylene)bis (1,3,4-oxadiazole-5,2-diyl)bis(sulfanediyl)dibenzenamine](**L$_3$**) (0.5 mmol). The reaction mixture was refluxed for 2 h. Then the mixture was left for 24 h to give a precipitate which was filtered off, washed with ethanol and diethyl ether.

17.3 Results and Discussion

The new ligands (**L$_1$**), (**L$_3$**) and (**L$_2$**) were prepared by the reaction of [5-phenyl-1,3,4-oxadiazole-2-thiol] and [5,5′-(1,4-phenylene)bis(1,3,4-oxadiazole-2-thiol)] with 2-aminothiophenol and [2-(5-phenyl-1,3,4-oxadiazole-2-ylthio)benzenamine] with isatin respectively. The complexes were prepared by the direct reaction of the metal chlorides, $NiCl_2.6H_2O$ or $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$ with the above ligands. All the metal complexes are coloured and are soluble in DMF and DMSO. Conductance measurements of the metal complexes in 10^{-3} M DMSO solution at room temperature suggested non-electrolytic nature for all the complexes. The yields, physical properties, analytical and spectral data of the ligands and their metal complexes are shown in Tables 17.1 and 17.2, respectively. The proposed structures of the metal complexes are shown in Fig. 17.5.

17.3.1 ^{1}H-NMR Data

The ^{1}H-NMR spectra of the ligands (**L$_1$**), (**L$_2$**) and (**L$_3$**) were recorded in deuterated DMSO solution. The results showed that the signals at δ 5.4 ppm for (**L$_1$**) and (**L$_3$**) ligands are due to the N-H protons. Aromatic ring protons appeared at δ 6.42, 6.50, 6.79 and 7.00 ppm for (**L$_1$**) ligand (Fig. 17.6) and at δ 6.40, 6.45, 6.74 and 7.00 ppm for (**L$_3$**) ligand (Fig. 17.7). Signals at δ 7.40, 7.21 and 7.11 ppm for (**L$_1$**) ligand and at δ 7.0-7.1 ppm for (**L$_3$**) ligand are due to the chemical shifts of aromatic ring protons linking the oxadiazole ring. The ^{1}H-NMR spectrum of (**L$_2$**) ligand showed a signal at δ 11.0 ppm due to the N-H proton of isatin. Aromatic ring

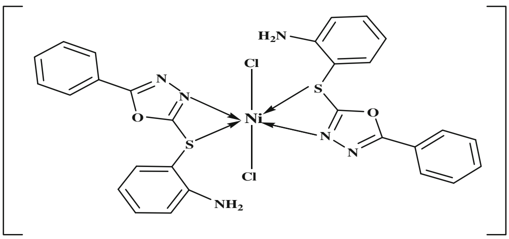
Table 17.1 Physical properties, analytical and spectral data of ligands

Ligand (formula)	Yield (%)	Colour M. P. (°C)	Band absorptions (cm^{-1} nm)	Molar conductivity ($\Omega^{-1}cm^2\ mol^{-1}$)	Selected IR bands (cm^{-1})				^{1}H-NMR (ppm)		
					v(NH_2)	*v*(C=N)	*v*(C–S)	*v*(C–O–C)	δ_{arom} (5H)	δ_{arom} (4H)	δ(N–H)
L_1 ($C_{14}H_{11}N_3OS$)	94	Light green 172–173	37878 (264) 32467 (308)	0.5	3379 (m) 3300(m)	1616 (s)	690 (s)	1062 (m)	7.1–7.4	6.4–7.0	5.4–5.9
L_2 ($C_{22}H_{14}N_4O_2S$)	79	Orange 154–156	38759 (258) 33334 (300)	5.5	3200 (m) 3400 (m)	1650 (m) 1614 (s)	684 (m)	1058 (m)	7.5–8.1	6.4–7.0 7.1–7.6	10.8–11.0
L_3 ($C_{22}H_{16}N_6O_2S_2$)	87	Light green 200–202	38461 (260) 29241 (340)	7.8	3305 (m) 3230 (m)	1620 (s)	698 (m)	1072 (s)	_	6.4–7.0 7.0–7.1	5.4

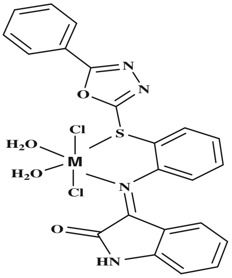
s = strong, *m* = medium

Table 17.2 Physical properties, analytical and spectral data of the complexes

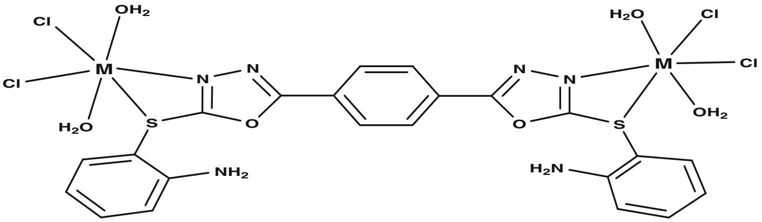
Complex (colour)	Yield (%) (Decom./°C)	Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	μ_{eff} (B.M.)	Band absorptions (nm)	Selected IR bands (cm^{-1})					
					ν(O–H)	ν(C=N)	ν(C–S)	ν(M–N)	ν(M–S)	ν(M–Cl)
$[Ni(L_1)_2Cl_2]$ (green)	63 (155–157)	11.8	3.3	292 453 557	–	1612 (s)	634 (w)	540 (w)	447 (w)	378 (m)
$[Ni(\mathbf{L_2})Cl_2(H_2O)_2]$ (greenish-brown)	68 (190–192)	16.4	3.2	437 560	3461 (b)	1654 (m) 1616 (s)	682 (s)	578 (w)	420 (w)	393 (w)
$[Co(\mathbf{L_2})Cl_2(H_2O)_2]$ (Dark brown)	56 (208–210)	12.4	4.1	280 451 559	3550 (b)	1652 (m) 1616 (s)	682 (s)	557 (w)	451(m)	370 (s)
$[Cu(\mathbf{L_2})Cl_2(H_2O)_2]$ (dark violet)	59 (215–217)	8.7	1.7	562	3419 (m)	1654 (m) 1616 (s)	676 (m)	526 (w)	453 (m)	390 (s)
$[Ni_2(\mathbf{L_3})Cl_4(H_2O)_4]$ (green)	75 (185–187)	13.0	3.7	390 441 532	3532 (s)	1614 (m)	619 (w)	532 (w)	441 (w)	381 (s)
$[Co_2(\mathbf{L_3})Cl_4(H_2O)_4]$ (dark blue)	62 (252–254)	11.7	4.2	427 560	3560 (s)	1616 (s)	678 (w)	526 (w)	433 (w)	378 (s)
$[Cu_2(\mathbf{L_3})Cl_4.(H_2O)_4]$ (dark green)	80 (240–242)	15.3	1.9	582	3548 (s)	1615 (s)	676 (m)	519 (m)	445 (m)	390 (s)



$[Ni(L_1)_2Cl_2]$



$[M(L_2)Cl_2(H_2O)_2]$ (M=Ni(II), Co(II) and Cu(II))



$[M_2(L_3)Cl_4(H_2O)_4]$ ((M=Ni(II), Co(II) and Cu(II))

Fig. 17.5 Proposed structures of the metal complexes

protons of isatin appeared at δ 7.61, 7.58, 7.33 and 7.09 ppm for (**L_2**) ligand. In addition there are other aromatic protons appearing at δ 6.99, 6.72, 6.55 and 6.35 ppm. The signals at δ 8.05, 7.89 and 7.48 ppm are assigned to aromatic ring protons bonded to oxadiazole. All the observed chemical shift values were within the values found in the literature [11, 12].

17.3.2 Infrared Spectral Studies

The infrared spectra of (**L_1**) (Fig. 17.8), (**L_2**) (Fig. 17.9) and (**L_3**) ligands showed bands in the range 3379–3300 cm^{-1}, 3200–3400 cm^{-1} and 3305–3230 cm^{-1} respectively, corresponding to ν(N–H) [13, 14]. Strong and broad bands in the range 3419–3560 cm^{-1} can be assigned to ν(O–H) of coordinated water molecules [15, 16]. A strong absorption at 1616, 1614 and 1620 cm^{-1} appeared in the

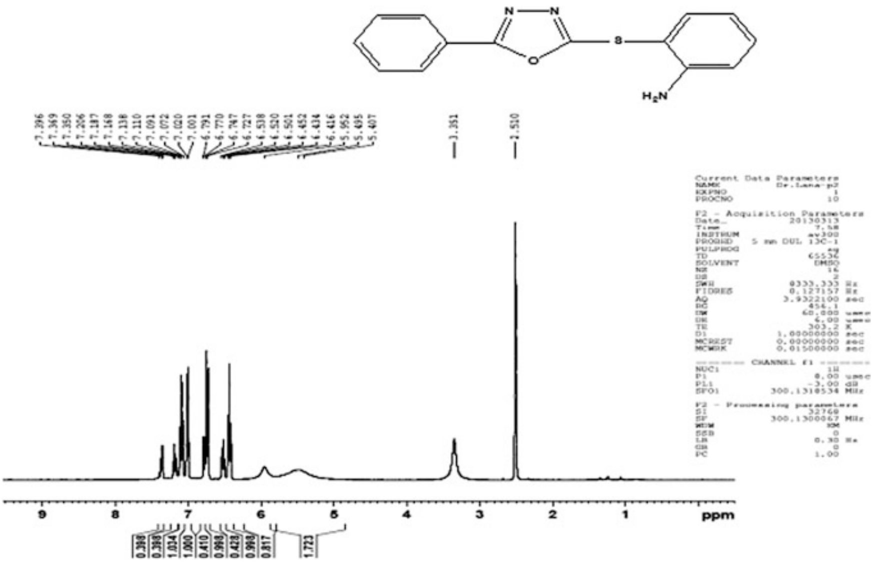


Fig. 17.6 ^{1}H-NMR spectrum of (**L$_1$**)

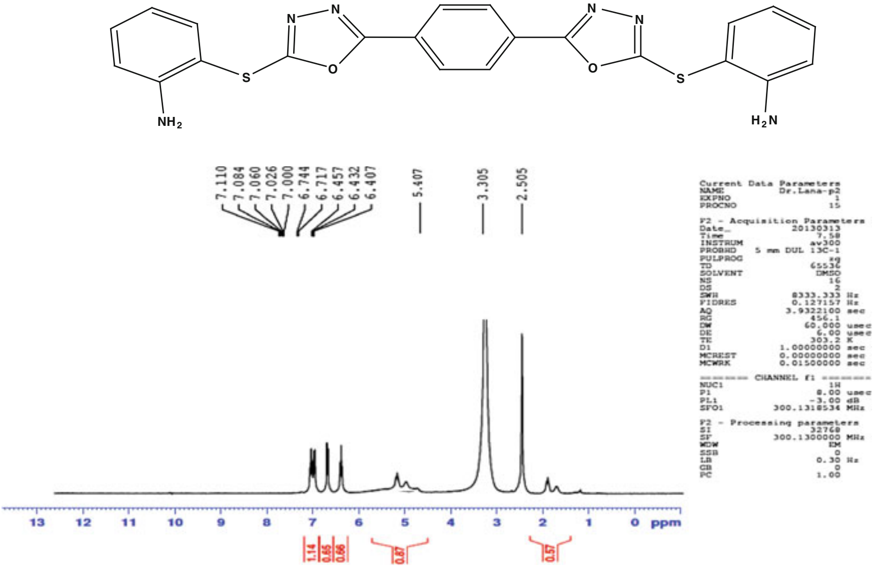


Fig. 17.7 ^{1}H-NMR spectrum of (**L$_3$**)

spectrum of (**L$_1$**), (**L$_2$**) and (**L$_3$**), respectively, due to the endocyclic *v*(C=N) of oxadiazole ring. The infrared spectra of two nickel complexes [Ni(**L$_1$**)$_2$Cl$_2$] and [Ni (**L$_2$**)$_2$Cl$_2$(H$_2$O)$_2$] are depicted in Figs. 17.10 and 17.11 respectively. A negative and

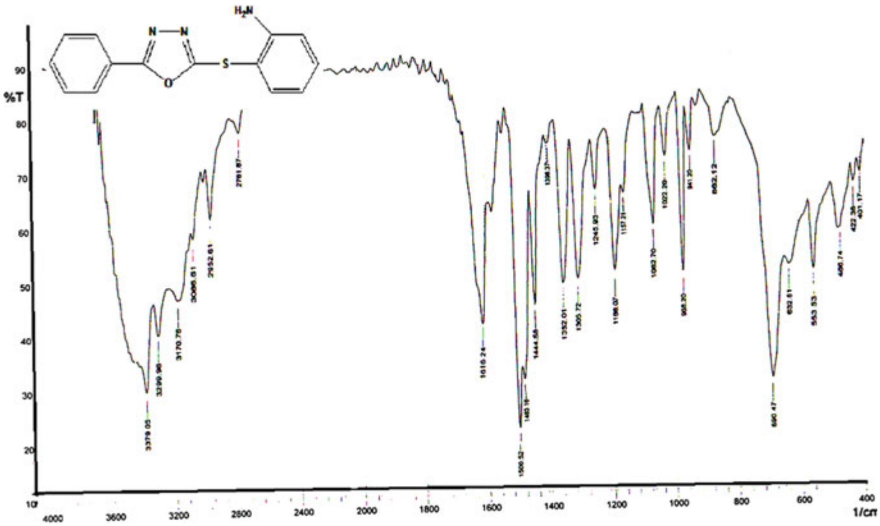


Fig. 17.8 Infrared spectrum of ($\mathbf{L_1}$)

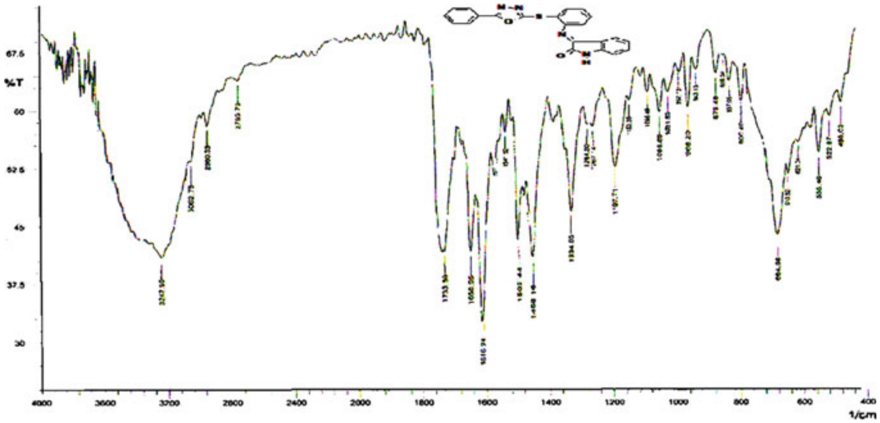


Fig. 17.9 Infrared spectrum of ($\mathbf{L_2}$)

positive shift in ν(C = N) of the chelates (1612-1654 cm^{-1}) suggest the involvement of nitrogen in coordination [17–19]. The ν(C–S) band of the free ligands in the range 698–684 cm^{-1} shifted to lower frequency (682–619 cm^{-1}) in the complexes, indicating coordination of (C–S) to the metal ions [15]. Further support came from the IR spectra of the complexes which showed new bands at 519–578 cm^{-1} attributed to ν(M–N) [17]. A band was also observed in the region 370–393 cm^{-1} which may be due to ν(M–Cl) [20]. Further support for this coordination has been provided by the appearance of new bands in the 420–453 cm^{-1} range which are attributed to ν(M–S) [21].

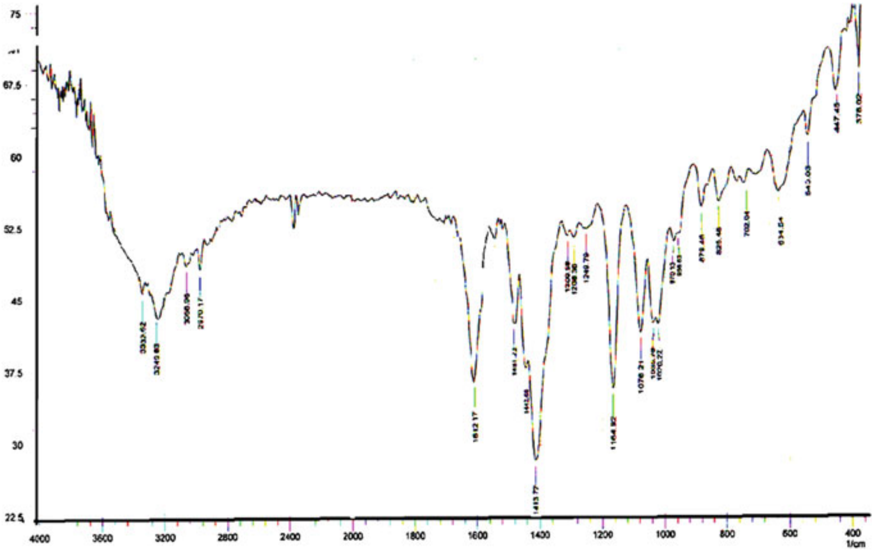


Fig. 17.10 Infrared spectrum of [Ni($\mathbf{L_1}$)$_2$Cl$_2$]

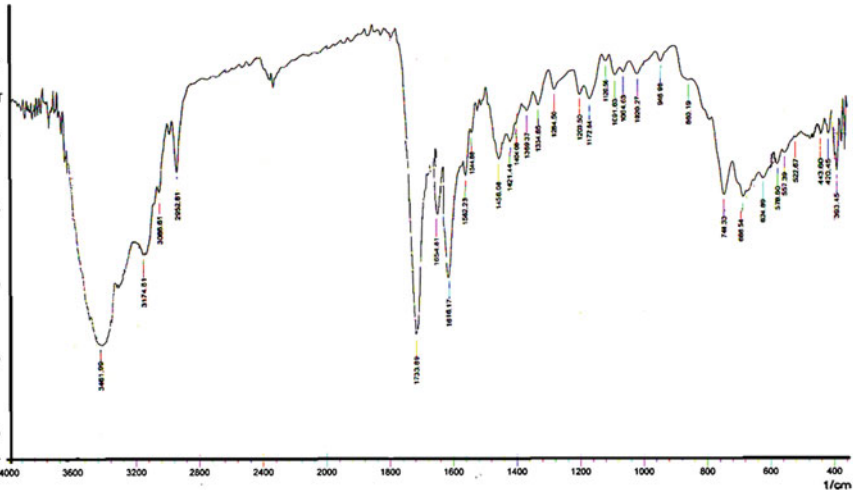


Fig. 17.11 Infrared spectrum of [Ni($\mathbf{L_2}$)$_2$Cl$_2$(H$_2$O)$_2$]

17.3.3 Magnetic Susceptibility Measurements

The magnetic moments were measured at 25 °C. The results indicated an octahedral geometry for Ni(II) (μ_{eff} = 3.2–3.7 B.M.), Co(II) (μ_{eff} = 4.1–4.2 B.M.) and Cu(II) (μ_{eff} = 1.7–1.9 B.M.) complexes, and compared favourably with similar octahedral complexes such as $Ni(L)Cl_2 \cdot H_2O$ (μ_{eff} = 3.0 B.M.), $Co(L)Cl_2 \cdot H_2O$ (μ_{eff} = 4.46 B.M.) and $Cu(L)(SO_4)_2 \cdot H_2O$ (μ_{eff} = 1.9 B.M.), where L = 2,2′-diimino-*N*-phenylhydrazobenzene. The number of unpaired electrons are 2, 3 and 1 for the Ni(II), Co(II) and Cu(II) complexes, respectively [22].

17.3.4 Electronic Spectral Studies

The electronic spectra of the ligands and their complexes in 10^{-3} M solution in DMSO were recorded and the results are listed in Table 17.2. The bands at 258–340 nm are due to π–π* and *n*–π* transitions in the ligands. The spectra of nickel (II) complexes showed bands at 390-560 nm, which are assigned to $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and $^3A_2g \rightarrow {}^3T_1g$ (F) transitions, consistent with proposed octahedral symmetry of these complexes [21]. The electronic spectra of Co(II) complexes showed bands at 427-560 nm assigned to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions in an octahedral environment around cobalt ion [23]. The high energy band observed around 280 nm may be assigned to M → L charge transfer transition [24]. The electronic spectra of Cu(II) complexes showed broad bands at 562–582 nm which were assigned to $^2B_{2g} \rightarrow {}^2E_g$ transition in a distorted octahedral environment [10].

17.4 Conclusions

The present work includes the synthesis of three new ligands of 1,3,4-oxadiazole derivatives, and seven complexes with these ligands. On the basis of IR, UV-Visible spectra, and magnetic susceptibility values, the complexes of Ni(II), Co (II) and Cu(II) metal ions are postulated to have most probably octahedral geometries, with the ligands chelated to the metal through S and N atoms. According to the molar conductivity data, all the synthesized complexes are found to be non-electrolytic in nature.

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