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Formation of new metal complexes with benzene triazole and thiadiazole-based Schiff-bases

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Abstract : The reaction of benzotriazole carbaldehyde with 5-(4-chloro-phenyl)-[1,3,4]thiadiazol-2-ylamine, and 5-(3-bromo-phenyl)-[1,3,4]thiadiazol-2-ylamine resulted in the formation of new tridentate ligands; benzotriazol-1-ylmethylene-[5-(4-chloro-phenyl)-[1,3,4]thiadiazol-2-yl]-amine L¹ and benzotriazol-1-ylmethylene-[5-(3-bromo-phenyl)-[1,3,4]thiadiazol-2-yl]-amine L², respectively. Monomeric complexes of general formulae [M(Lⁿ)Cl] (where; M = Co(II), Ni(II), Zn(II)) were obtained from the reaction of these ligands with Co(II), Ni(II) and Zn(II) metal ions. The mode of bonding and overall geometry of the complexes were determined through IR, UV-Vis, NMR, magnetic

moment measurements, elemental analysis, metal content, chloride content and conductance. The IR data revealed that the nitrogens of the Schiff-base and that of triazole moiety are coordinated to metal ion, in a tridentate fashion. The physico-chemical studies revealed the formation of four-coordinate complexes with distorted square planar for Co(II), and Ni(II) and five coordinate complex with Zn(II).

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Keywords : Benzotriazole carbaldehyde; 5-(4-Chloro-phenyl)-[1,3,4]thiadiazol-2-ylamine, and 5-(3-Bromo-phenyl)-[1,3,4]thiadiazol-2-ylamine; Metal complexes; Structural study.

INTRODUCTION

The coordination chemistry of nitrogen-sulfur containing heterocyclic ligands, such as 1,2,4-triazoles, 1,3,4-oxadiazoles and 1,3,4-thiadiazoles, is an interesting and rapidly developing area of re-

search^[1-3]. These compounds have drawn the attention of researchers due to their important pharmacological activities^[4]. Triazole derivatives have been used as starting materials to fabricate a variety of drug-based compounds and also act as ligands to obtain metal complexes that have specific proper-

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ties^[5]. Oxadiazole and 1,3,4-thiadiazole derivatives bearing an important group of heterocyclic compounds that have diverse biological activities, such as anti-tuberculostatic, anti-inflammatory, analgesic, antipyretic, anticonvulsant, antibacterial and antifungal activities^[6-8]. 1,2,4-Triazoles with amino groups on the backbone are potential materials for obtaining various Schiff-base derivatives with well known antimicrobial properties^[9-11]. Polyazoles, imazoles and triazoles ligands have been extensively used to construct various coordination networks with diverse topologies and interesting properties^[13,14]. The structure and properties of metal complexes depend on the metal ion and the donor atoms, as well as the structure of the ligand and the metal-ligand interactions^[15]. The good choice or design of organic ligands coupled with suitable metal ions may lead to complexes with specific structures and properties^[16]. Great efforts have been focused on ligands based on azoles heterocycles which have both good coordination ability and diverse coordination modes^[17]. In this paper, we report the preparation of new tridentate ligands benzotriazol-1-ylmethylene-[5-(4-chloro-phenyl)-[1,3,4]thiadiazol-2-yl]-amine (L^1) and benzotriazol-1-ylmethylene-[5-(3-bromo-phenyl)-[1,3,4]thiadiazol-2-yl]-amine (L^2), and their complex formation with some metal ions. The aim of this work is to examine the influence imposed on the geometry of complexes upon using two types of azole triazole and thiadiazole moieties.

EXPERIMENTAL

Materials and methods

Reagents were obtained commercially and used without further purification. Solvents used in the synthesis were distilled from appropriate drying agent immediately prior to use.

Physical measurements

Elemental analyses (C, H, N) were carried out on a Heraeus instrument (Vario EL). IR spectra in the range 4000-400 cm^{-1} were recorded as KBr discs using a Shimadzu 8400 S FTIR spectrophotometer. Electronic spectra were measured from 200-1100 nm for 10^{-3} M solutions in DMSO at 25°C using a

Shimadzu 1800 spectrophotometer. Mass spectra for ligands and some metal complexes were obtained by positive Electrospray (ES) mass using a Thermo LTQ Orbitrap XL spectrometer. ^1H - ^{13}C -NMR spectra were acquired in DMSO- d_6 solution using a Jeol 400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^1H NMR analysis. Melting points were obtained on an Electro-thermal Stuart melting point SMP40 capillary melting point apparatus and are uncorrected. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride content was determined using potentiometer titration method on a 686-Titrip processor-665Dosimat-Metrohm Swiss. Conductivity measurements were made with DMSO solutions using a PW 9526 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Johnson Matthey Catalytic Systems Division).

Synthesis

Preparation of ligands

The ligands were prepared using a standard method reported in^[13] and as follows:

Preparation of L^1

A mixture of thiosemicarbazide (0.4557g, 0.01mol) and (0.78g, 0.01mol) of p-chlorobenzoic acid with (10 ml) of phosphorous oxychloride was allowed to reflux for 7 h. The reaction mixture was kept at room temperature, and then diluted with 25 ml of water before heated at reflux for 8 h. The reaction solution was allowed to cool at RT, and then neutralized with 10% of KOH. The deep yellow precipitate was filtered off and recrystallised from hot methanol. The product 5-(4-chloro-phenyl)-[1,3,4]thiadiazol-2-ylamine then reacted with 1 equivalent of benzotriazole carbaldehyde in methanol medium and refluxed for 2 h. Solvent was removed under reduced pressure, and precipitate was formed, which washed with water (5 mL). The solid product was recrystallised with a mixture of EtOH/water, and then washed with (5 mL) of diethyl ether and dried in vacuo. Yield: 0.24 g (73%) of the title compound, m.p. = 242-244 °C. NMR data (ppm), δ_{H} (300 MHz, DMSO- d_6): 7.054 (2H, C_{12'}, C_{14'}-H),

7.540 (2H, C_{11,15}-H), 7.858 (2H, C_{2,3}), 8.178 (1H, C₇), 8.348 (2H, C_{1,4}). δ_C (100.63 MHz, DMSO-d₆): 119.12 (C_{11,15}), 122.45 (C_{1,2,3,4}), 123.72 (C_{12,14}), 124.19 (C_{5,6}), 129.24 (C₁₃), 132.49 (C₁₀), 155.36 (C₇), 170.05 (C₈), (see supporting information, Figures SI 11, 12). The mass spectrum of L¹ showed several peaks corresponding to successive fragmentations of the molecule. Peak detected at m/z 340.39 (16%) (M)⁺ represents the molecular ion peak of L¹ ligand. Other distinct peaks were observed in the spectrum at m/z 222.11 (100 %) which represents the molecular ion peak of the ligand losing benzotriazole moiety [M-(C₆H₄N₃)]⁺. Peak detected at 198.09 (15 %) refer to losing [M-(C₆H₄N₃+HC=N)]⁺. The last peak detected at 111.02 (21%) assigned to the [M-(C₆H₄N₃+HC=N+C₂H₂N₂S)]⁺ fragment (see supporting information, Figure SI 9).

Preparation of L²

The method used to prepare L² was analogous to that reported for L¹, but with (0.5g, 0.01mol) of m-bromobenzoic acid instead of p-chlorobenzoic acid. Other reagents were adjusted accordingly. A similar work-up procedure was used to obtain 5-(3-bromo-phenyl)-[1,3,4]thiadiazol-2-ylamine, which then reacted with 1 equivalent of benzotriazole carbaldehyde in methanol. The required compound was obtained as a pale yellow precipitate. Yield: 1.43 g (68%), m.p 266-268 °C. NMR data (ppm), δ_H (400 MHz, DMSO-d₆): 7.46 (2H, C_{12,14}-H), 7.51 (2H, C_{11,15}-H), 7.78 (2H, J=7.33 Hz, C_{2,3}), 8.14 (1H, C₇), 8.27 (2H, C_{1,4}). δ_C (100.63 MHz, DMSO-d₆): 123.28 (C₁₄), 125.16 (C₁₁), 128.13 (C_{1,2,3,4}), 129.24 (C_{5,6}), 133.72 (C₁₃), 137.70 (C₁₂), 161.34 (C₇), 166.96 (C₈), (see supporting information, Figures SI 13, 14). The negative mass spectrum of L² showed several peaks corresponding to successive fragmentations of the molecule. Peak detected at m/z 384.98 (7 %) (M-1)⁺ represent the molecular ion peak of the ligand losing only one hydrogen atom. Other distinct peaks observed in the spectrum at m/z 265.28 (15 %), 239.09 (5 %) and 154.07 (100%) refer to [M-(C₆H₄N₃)]⁺, [M-C₆H₄N₃+HC=N]⁺ and [M-C₆H₄N₃+HC=N+C₂H₂N₂S]⁺ fragments, respectively (see supporting information, Figure SI 10).

General synthesis of complexes with L¹ and L² ligands

A solution of the appropriate ligand (1 mmol) in ethanol (20 ml) was allowed to stir for 30 min, and then a solution of metal chloride (1 mmol) in ethanol (5 ml) was added drop-wise. The reaction mixture was refluxed for 2 h. The coloured solid that formed was filtered off, washed with acetone (10 ml), and dried in vacuo. Elemental analysis data, colours, and yields for the complexes are given in (TABLE 1).

RESULTS AND DISCUSSION

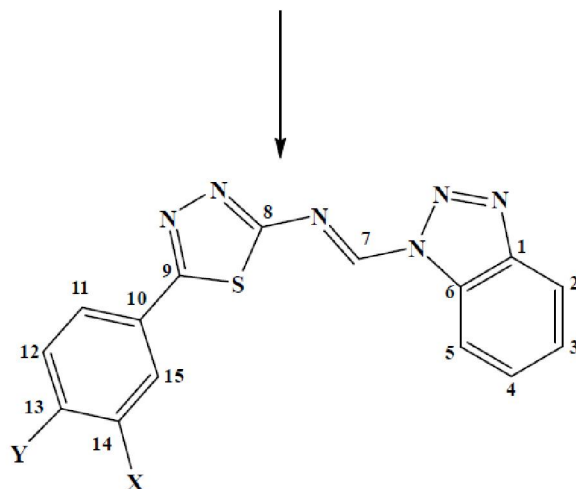
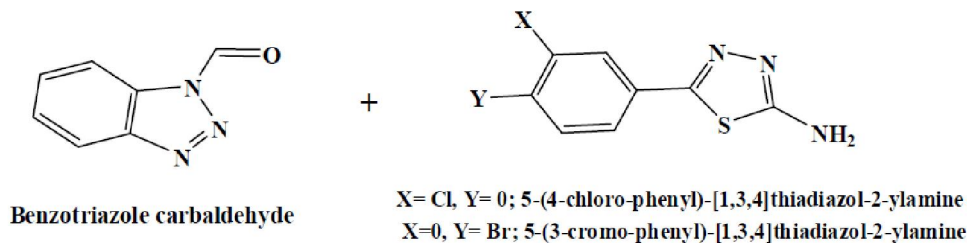
Chemistry

The new benzene triazole Schiff-base ligands, L¹ and L², were obtained in good yields by the reaction of benzene triazole carboxyldehyde with 5-(4-chloro-phenyl)-[1,3,4]thiadiazol-2-ylamine and 5-(3-bromo-phenyl)-[1,3,4]thiadiazol-2-ylamine, respectively (see Scheme 1). The ligands were prepared in a similar fashion in methanol medium. The ligands were characterised by elemental analysis (TABLE 1), IR (TABLE 2), UV-Vis (TABLE 3), ¹H, ¹³C NMR spectroscopy and mass spectra. The complexes were prepared from the reaction of the ligands with Co(II), Ni(II) and Zn(II), by heating 1 mmole of each ligand with 1 mmole of metal chloride, using ethanol solvent. Elyctrolyte complexes of the general formulae [M(Lⁿ)Cl]Cl (M = Co(II) and Ni(II)) and neutral [M(Lⁿ)Cl₂] (M = Zn(II); n =1 or 2) were obtained (Scheme 2). The complexes are air-stable solids, soluble only in hot DMF and DMSO with stirring, and not soluble in other common organic solvents. Spectral data were used to figure out the coordination geometries of the complexes. The analytical data (TABLE 1) agree well with the suggested formulae. The most important infrared bands of the ligands and their complexes together with their assignments are collected in (TABLE 2). The electronic spectra for the ligands and their complexes are presented in (TABLE 3).

IR and NMR spectra

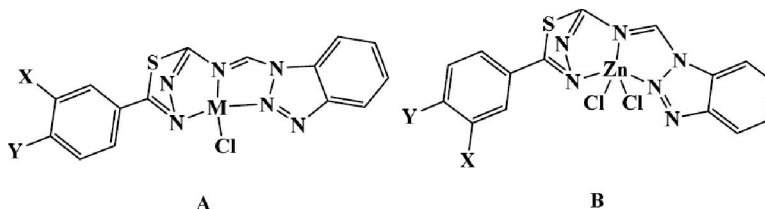
The important infrared bands for the ligands and their complexes together with their assignments are

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Where: $\text{X} = 0 = \text{L}^1, \text{Y} = \text{Cl}$
 $\text{Y} = 0 = \text{L}^2, \text{X} = \text{Br}$

Scheme 1 : General synthetic route for ligands



Where: $\text{X} = 0 = \text{L}^1, \text{Y} = \text{Cl}$
 $\text{Y} = 0 = \text{L}^2, \text{X} = \text{Br}$
 $\text{M} = \text{Co(II)}, \text{Ni(II)}$

Scheme 2 : General structure for the proposed complexes

listed in (TABLE 2). The IR spectra of the free ligands show characteristic bands due to the imine $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ functional groups. Bands detected around 1614 and 1641 cm^{-1} are due to the $\nu(\text{C}=\text{N})$ in L^1 and L^2 , respectively (see supporting information, Figures SI 1, 2)^[18, 19]. Peaks at 1602 , 1473 in L^1 and 1612 , 1486 in L^2 are due to $\nu(\text{C}=\text{C})$. Bands recorded at 1328 , 856 and 1376 , 853 cm^{-1} are attributed to $(\text{C}-\text{S})$ in L^1 and L^2 , respectively^[20]. The IR spectra show bands at 1107 and 1082 which can be attributed to $\nu(\text{N}=\text{N})$ group in L^1 and L^2 , respectively^[21].

The IR spectra of the complexes exhibited ligand

bands with the appropriate shifts due to complex formation (TABLE 2). The $\nu(\text{C}=\text{N})$ imine bands were appeared at lower frequency and observed in the range 1606 - 1610 and 1620 - 1634 cm^{-1} , for L^1 and L^2 , respectively (compared with that detected in the free ligands at 1614 and 1641 cm^{-1} in L^1 and L^2 , respectively). The shift of these bands to lower frequencies is due to reduced bond order in L^1 and L^2 . This can be attributed to delocalisation of metal electron density (t_{2g}) to the π -system of the ligand^[22], indicating coordination nitrogen of imine group and nitrogen of the triazole moieties to the metal atoms. The $\nu(\text{C}-\text{S})$ of the thiadiazole groups is detected in the

TABLE 1 : Colours, yields, elemental analyses, and molar conductance values

Compound	Colour	Yield (%)	m.p	Found (Calcd.) (%)				Total halide (Cl/Br)	$\Lambda_M(\text{cm}^2\Omega^{-1}\text{mol}^{-1})$
				M	C	H	N		
L ¹	Yellow	78	218	-	52.07 (52.87)	2.34 (2.66)	24.26 (24.66)	9.76 (10.40)	-
[Co ^{II} (L ¹)Cl]Cl	Blue	65	287	12.28 (12.52)	37.87 (38.28)	1.91 (1.93)	17.22 (17.86)	22.35 (22.60)	32.13
[Ni ^{II} (L ¹)Cl]Cl	Green	74	279*	12.07 (12.48)	38.12 (38.30)	1.84 (1.93)	17.67 (17.87)	22.17 (22.61)	35.78
[Zn ^{II} (L ¹)Cl ₂]	Yellow	82	253*	13.04 (13.71)	37.27 (37.76)	1.87 (1.90)	17.04 (17.61)	21.83 (22.29)	6.24
L ²	Dark yellow	73	267	-	45.95 (46.77)	2.24 (2.35)	21.57 (21.81)	20.17 (20.74)	-
[Co ^{II} (L ¹)Cl]Cl	Blue	79	289*	11.26 (11.44)	34.83 (34.98)	1.73 (1.76)	16.12 (16.32)	28.93 (29.28)	36.82
[Ni ^{II} (L ¹)Cl]Cl	Green	68	288*	11.16 (11.40)	34.83 (34.99)	1.68 (1.76)	16.09 (16.32)	28.87 (29.29)	33.46
[Zn ^{II} (L ¹)Cl ₂]	Yellow	77	285	6.89 (7.07)	38.61 (38.96)	11.65 (12.18)	17.81 (18.17)	24.27 (24.95)	5.07

* Decomposed

same region that observed in the free ligands, indicating the non coordination to metal ion in L¹ and L². Bands at 1107-1080 cm⁻¹ attributed to $\nu(\text{N}=\text{N})$ ^[21] in L¹ complexes, while 1151-1022 cm⁻¹ in L² complexes. The bands at 1007-1016 cm⁻¹ assigned to $\nu(\text{N}-\text{N})$. The fashion and the shape of the bands refer to the coordination of the imine moieties to the metal atoms^[23]. Further, the IR spectra of the complexes display characteristic bands for $\nu(\text{M}-\text{N})$ vibration mode around 426-565 and 435-499 cm⁻¹ which assigned to two type of $\nu(\text{M}-\text{N})$ of imine and triazole nitrogen in L¹ and L², respectively (see supporting information, Figures SI 3-8)^[24]. These bands indicated that the imine nitrogen and the triazole of benzotriazole for the ligands are involved in coordination with metal ion.

The ¹H and ¹³C NMR spectra of the ligands displayed signals corresponding to the various protons and carbons nuclei (See Experimental section). The ¹H NMR spectra of the ligands displayed signals corresponding to the various protons. The spectrum show peak around 7.054 ppm assigned to (-CH) group (2H, C_{12,14}-H) of the aromatic ring proton, which appear at high chemical shift due to effect of chloro group, the chemical shift at 7.540 assigned to

(2H, C_{11,15}-H) appear at down field due to effect of neighbouring thiadiazole group, the signal at 7.858 may be due to (2H, C_{2,3}), the appearance the chemical shift at high chemical shift due to benzotriazole of carbaldehyde group, the signal that appear in down field at 8.178 (1H, C₇) assigned to imine group which deshielding, 8.348 (2H, C_{1,4}), (see supporting information, Figure SI 11). δ_C (100.63 MHz, DMSO-d₆): the signal at 119.12 assigned to (C_{11,15}) due to neighbouring of thiadiazole ring, 122.45 (C_{1,2,3,4}), the signal at 123.72 (C_{12,14}) due to neighbouring electron with drawing chloro group, 124.19 (C_{5,6}), the chemical shift at 129.24 (C₁₃) which appear at high chemical shift due to attached the carbon atom by chloro, 132.49 (C₁₀), the signal at 155.36 (C₇) appear in down field due to deshielding of carbon atom by the effect of double bond of imine group, 170.05 (C₈), (see supporting information, Figure SI 12).

L²: 7.46 (2H, C_{12,14}-H), 7.51 (2H, C_{11,15}-H), 7.78 (2H, $J=7.33$ Hz, C_{2,3}), 8.14 (1H, C₇), 8.27 (2H, C_{1,4}), (see supporting information, Figure SI 13). δ_C (100.63 MHz, DMSO-d₆): 123.28 (C₁₄), 125.16 (C₁₁), 128.13 (C_{1,2,3,4}), 129.24 (C_{5,6}), 133.72 (C₁₃), 137.70 (C₁₂), 161.34 (C₇), 166.96 (C₈), (see

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supporting information, Figure SI 14).

Electronic spectra, magnetic moments and conductivity measurements

The UV–Vis spectra of L¹ and L² show peaks at 245 and 265 nm, respectively and at 305 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The electronic spectra of the complexes of L¹ exhibited various extents of hypsochromic shift of the bands related to the intra-ligand $\pi \rightarrow \pi^*$ transi-

tion. The electronic spectra of the Co(II) and Ni(II) complex are consistent with square planar assignment^[24-26]. The magnetic moment of Co-complex is typical for a low spin square planar structure. The Ni(II) complex is diamagnetic suggesting a square planar geometry^[27-30]. The electronic spectrum of this complex, as well as the other analytical data, was consistent with this assignment. The spectrum of the Zn(II) complex exhibited band assigned to intraligand $\pi \rightarrow \pi^*$ ^[24]. This complex is diamagnetic as expected,

TABLE 2 : IR frequencies (cm⁻¹) of the compounds

Compound	$\nu(\text{CH})_{\text{aro}}$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{N}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{N})$
L ¹	3055	1614	1602, 1473	1222	1328, 856	1107	1007	-
[Co ^{II} (L ¹)Cl]Cl	3061	1606	1606, 1490	1221	-	1080	1010	426, 459
[Ni ^{II} (L ¹)Cl]Cl	3035	1610	1610, 1493	1220	1330, 851	1083	1016	428, 460
[Zn ^{II} (L ¹)Cl ₂]	3063	1609	1609, 1492	1224	1342, 856	1080	1011	498, 565
L ²	3047	1641	1612, 1486	1225	1376, 853	1082	930	-
[Co ^{II} (L ²)Cl]Cl	3065	1620	1603, 1487	1224	1368, 833	1151	1010	436, 499
[Ni ^{II} (L ²)Cl]Cl	3038	1634	1611, 1468	1230	1348, 845	1045	1002	435, 486
[Zn ^{II} (L ²)Cl ₂]	3048	1632	1597, 1458	1218	1369, 841	1022	963	440, 476

TABLE 3 : Magnetic moment, and u.v-vis spectral data in DMSO solutions

Compound	μ_{eff} (BM) (per atom)	Band position (λ_{nm})	Extinction coefficient ϵ_{max} (dm ³ mol ⁻¹ cm ⁻¹)	Assignments
[Co ^{II} (L ¹)Cl]Cl	1.82	245	631	L.F
		305	1066	intraligand
		370	800	C.T
		422	570	² E _g → ² T _{2g}
		650	70	² E _g → ² T _{1g}
[Ni ^{II} (L ¹)Cl]Cl	Diamagnetic	260		Intraligand
		350		C.T
		425	1053	¹ A _{1g} → ¹ B _{1g}
		510		¹ A _{1g} → ¹ A _{2g}
		265	1744	Intraligand
[Zn ^{II} (L ¹)Cl ₂]	Diamagnetic	370	800	C.T
		423	1055	C.T
[Co ^{II} (L ²)Cl]Cl	1.83	240	861	$\pi \rightarrow \pi^*$
		315	1307	$n \rightarrow \pi^*$
		347	1170	C.T
		421	61	² E _g → ² T _{2g}
		626	63	² E _g → ² T _{1g}
[Ni ^{II} (L ²)Cl]Cl	Diamagnetic	245	1924	L.F
		265	744	Intraligand
		370	1189	C.T
		422	156	¹ A _{1g} → ¹ B _{1g}
		525	142	¹ A _{1g} → ¹ A _{2g}
		260	1443	Intraligand
[Zn ^{II} (L ²)Cl ₂]	Diamagnetic	280	1865	Intraligand
		345	1240	C.T
		422	100	C.T

d¹⁰ system. The analytical data was consisted with the formation of a complex in which the geometry about Zn atom is trigonal bipyramidal. This is in accordance with Zn-complexes reported previously^[31, 32]. The electronic spectra of the complexes of L² exhibited bands related to the intra-ligand $\pi \rightarrow \pi^*$ and the CT transitions (see TABLE 3). The spectra of the Co(II) and Ni(II) complexes of L² showed similar trend to those of L¹ suggesting square planar geometries for the complexes. The magnetic moment values were consistent with the square planar structures. The spectrum of Zn(II) complex of L² showed similar behaviour to those of L¹ suggesting trigonal bipyramide geometry^[26]. *The molar conductivity measurements indicate that both Co(II) and Ni(II) complexes are 1:1 electrolyte, while measurements revealed non-electrolyte for Zn(II)-complexes (see TABLE 1)^[33].*

CONCLUSION

In this paper, we have investigated the synthesis and coordination chemistry of some complexes obtained from the reaction of Schiff-bases with triazole-thiadiazole moieties with some metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. These studies revealed the formation of complexes bearing mixed tri-thia diazole moieties. In Co(II) and Ni(II) complexes, the geometries about metal centre is distorted square planar. On the other hand, a trigonal biipyramidal geometry has suggested for n-complexes.

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