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Synthesis and Characterization of Some New Antimicrobial Transition *Metal* Complexes with 1, 2, 4-Traizole-3-thione Schiff Bases

A. M. Hammam , M. A. EL-Gahami, Z. A. Khafagi, M. S. AL-Salimi and S. A. Ibrahim*
Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt, 71516 **.**

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**Corresponding Author. E-mail: saidibrahim7@yahoo.com*

Abstract

Co(II), Ni(II), Cu(II) and Cd(II) complexes of bidentate Schiff bases derived from the condensation of 4-amino-5-benzyl-4H-1,2,4-triazoles-3-thione with pyridine-2-carboxyaldehyde, pyridine-3-carboxya- ldehyde and pyridine-4-carboxyaldehyde were synthesized. The Schiff bases and their metal complexes were characterized by elemental and thermogravimetric analyses, spectral measurements (FT-IR, UV-Vis), molar conductance and magnetic moment measurements. Square planar (Cu(II) complexes), tetrahedral (Cd(II) complexes) and octahedral (Co(II) and Ni(II) complexes) geometries have been proposed. The presence of coordinated water in the metal complexes is confirmed by thermal analysis and IR data. The Schiff bases act as bidentate ligands coordinating via the azomethine nitrogen and thiolate sulfur atoms. The Schiff bases and their metal complexes have been screened for antimicrobial activity against six bacteria, namely *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus cereus*, *Micrococcus luteus*, *Escherichia coli and Serratia marcescens* and six fungi, namely *Candida albicans*, *Geotrichum candidum*, *Fusarium oxysporum*, *Scopulariopsis brevicaulis*, *Aspergillus flavus*, *and Trichophyton rubrum*.

Keyword: Triazole thione Schiff base complexes, antibacterial activity, thermogravimetric analyses.

Introduction

Metal complexes with Schiff base ligands have played an important role since the early days of coordination chemistry [1]. Schiff base ligands and their complexes may constitute such a possible class exhibiting biological activities [2-5] as well their structural analogues, compounds containing acyclic and cyclic imines are of great importance in modern coordination chemistry as they easily form stable complexes with most transition metal ions [6,7]. The five membered rings containing three nitrogen atoms are more important, since they act as ligands in most of the known hemoproteins. The utilization of the 1,2,4-triazole moiety as a part of ligand system in metal complexes has gained considerable attention in recent years [8-11]. Triazole complexes with some transition metals were found to exhibit antitumer activity [12,13] and also significant antifungal and antibacterial properties [14]. Generally metal complexes of ligands such as S,N-heterocycles exhibit enhanced biological activities compared to the uncomplexed ligand [15].

The work in the present paper is devoted to the synthesis and antimicrobial properties of Co(II), Ni(II), Cu(II) and Cd(II) metal complexes with Schiff bases derived from 3-substituted-4-amino-5-benzyl-4H-1,2,4-triazoles-3-thione derivatives. These Schiff bases contain the thioamide group which capable of undergoing (thione $\rightleftharpoons$ thiol) tautomerism and can be coordinated to the metal atom through both nitrogen and sulphur atoms. The structural features of Schiff bases and their metal complexes have been elucidated by various spectral and analytical techniques.

Materials and Methods

All the chemicals used were of reagent grade. 4-amino-5-benzyl-4H-1,2,4-triazoles-3-thione was synthesized according to the literature procedures [16-18].

Synthesis of 1, 2, 4 -Triazole-3-thione Schiff bases

A mixture of 4-amino-5-benzyl-4H-1,2,4-triazoles-3-thione (0.01 mol) and the following heterocyclic aldehydes (Fig. 1); pyridine-2-carboxyaldehyde, pyridine-3-carboxyaldehyde and pyridine-4-carboxyal- dehyde (0.01 mol) were dissolved in glacial acetic acid (5.0 mL). The reaction mixture was refluxed for 20 min. Then the mixture was cooled and the formed solid was filtered and washed with ethanol and recrystallised from ethanol and dried in vacuum over P_4O_{10} [19]. The corresponding Schiff bases are: 4-(2-pyridylmethelenamino)-3-mercapto-5-benzayl-1,2,4-triazole L_1: m.p = 192-194 °C, yield 64 %. The purity of the L_1 was

confirmed by elemental analysis Found (Calcd.)% for $C_{15}H_{13}N_5S$ (L_1) M.wt = 295.08; C, 60.74 (60.99); H, 4.05 (4.43); N, 23.20 (23.72); S, 11.02 (10.83).

4-(3-pyridylmethelenamino)-3-mercapto-5-benzayl-1,2,4-triazole L_2: m.p = 214-216 °C, yield 76 %. The purity of the L_1 was confirmed by elemental analysis Found (Calcd.) % for $C_{15}H_{13}N_5S$ (L_2) M.wt = 295.08; C, 60.38 (60.99); H, 4.44 (4.43); N, 23.47 (23.72); S, 10.09 (10.83).

4-(4-pyridylmethelenamino)-3-mercapto-5-benzayl-1,2,4-triazole (L_3) m.p = 234-236 °C, yield 72 %. The purity of the L_3 was confirmed by elemental analysis Found (Calcd.) % for $C_{15}H_{13}N_5S$ (L_3) M.wt = 295.08; C, 60.22 (60.99); H, 4.08 (4.43), N, 23.28 (23.72), S, 10.06 (10.83).

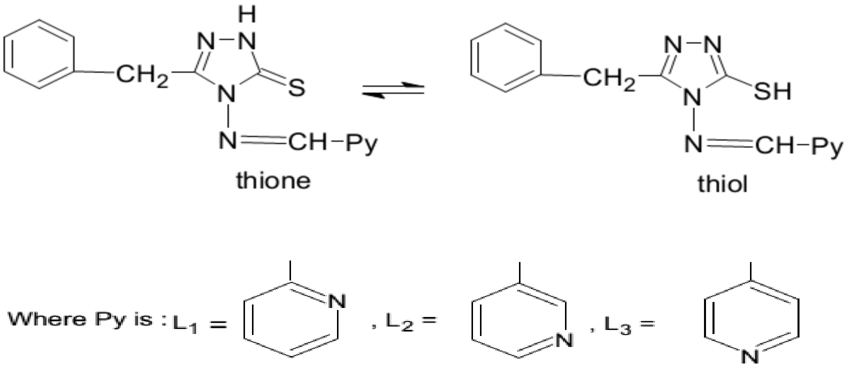


Figure 1: Structure of Schiff bases.

Synthesis of Co(II), Ni(II), Cu(II) and Cd(II) complexes

Hot ethanolic solution (40 ml) of Schiff bases (1mmol) was mixed with ethanolic solution (10 ml) of $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ and $CdCl_2.2.5H_2O$ (1 mmol), with constant stirring four 4 hours. Immediate precipitate was obtained in all cases. The products so obtained were left overnight, filtered through sintered glass, washed with ethanol and dried in vacuum over P_4O_{10}.

Antimicrobial activity of the ligands and their complexes

The antimicrobial activity of the free ligands and their binary metal complexes was tested against six bacterial and six fungal strain. All microbial strains were kindly provided by the Assiut University Mycological Center (AUMC). These strains are common contaminants of

the environment in Egypt and some of which are involved in human and animal diseases. The bacteria are: *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus cereus, Micrococcus luteus, Escherichia coli and Serratia marcescens* and the fungi are: *Candida albicans*, *Geotrichum candidum*, *Fusarium oxysporum Scopulariopsis brevicaulis*, *Aspergillus flavus and Trichophyton rubrum*. To prepare inocula for bioassay, bacterial strains were individually cultured for 48 h in 100ml conical flasks containing 30 ml nutrient broth medium. Fungi were grown for 7 days in 100 ml conicals containing 30 ml Sabouraud's dextrose broth. Bioassay was done in 10 cm sterile plastic in which microbial suspension (1 ml/plate) And 15ml appropriate agar medium (15ml/plate) were poured. Nutrient agar and Sabouraud's dextrose agar were respectively used for bacteria and fungi. After solidification of the media, 5 mm diameter cavities were cut in the solidified agar (4 cavities/plate) using sterile cork borer. Chemical compounds dissolved in dimethylformamide (DMF) at 2 %w/v (20 mg /ml) were pipetted in the cavities (20 µl/cavity). Cultures were then incubated at 20 °C for 24 h in case of bacteria and up to 7 days in case of fungi. Results were read as the diameter (in mm) of inhibition zone around cavities [20].

Physical measurements

Elemental analysis (carbon, hydrogen, nitrogen and sulphur) were performed using Analyischer Funktionstest VarioEL Fab-Nr.11982027 elemental analyzer. Infrared spectra were recorded as KBr disks (400-4000 cm^{-1}) with an FT-IR spectrophotometer model (Thermo-Nicolet-6700 FT-IR) and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. Magnetic susceptibility measurements were done on a magnetic susceptibility balance of the type MSB-Auto. The calibrant used was $Hg[Co(SCN)_4]$. The conductance was measured using a conductivity meter model 4310 JENWAY in DMF solutions at 10^{-3} M concentrations at room temperature (25 °C). Thermal studies were carried out in dynamic air on a Shimadzu DTG 60-H thermal analyzer at a heating rate of $10^{\circ}C\ min^{-1}$.

Results and discussion

The analytical data of the metal complexes are given in (Table 1). The data reveal the formation of complexes having 1:1 and 1:2 (metal ion : ligand). The data clearly indicate that, the ligands used act as neutral bidentate. The complexes are colored except all Cd(II) complexes are white. The complexes are insoluble in common organic solvents but all complexes completely soluble in DMF and DMSO.

Table 1. Analytical and physical data for the binary complexes of divalent transition metals complexes

	Complexes [Empirical formula] (Formula weight)	Analytical Data %Found (Calculated)						
		Color	C	H	N	S	Λ_0 $Ohm^{-1}cm^2mol^{-1}$	μ_{eff} B.M
1	$[Co(L_1)Cl_2\ (H_2O)_2]$ $(CoCl_2\ C_{15}H_{17}N_5SO_2\ )$ M.wt. = 459.97	brown	39.52 (39.13)	3.09 (3.72)	15.45 (15.22)	6.95 (6.95)	17.0	4.47
2	$[Co(L_2)_2Cl\ H_2O]Cl\ 2H_2O$ $(CoCl_2\ C_{30}H_{32}N_{10}S_2O_3)$ M.wt. = 773.08	blue	45.78 (46.56)	3.95 (4.17)	17.83 (18.11)	7.86 (8.26)	66.4	5.21
3	$[Co(L_3)_2Cl\ H_2O]Cl$ $(CoCl_2\ C_{30}H_{28}N_{10}S_2O)$ M.wt. = 737..07	blue	48.59 (48.84)	3.08 (3.82)	18.64 (18.99)	8.11 (8.67)	80.0	4.3
4	$[Ni(L_1)Cl_2]\ 0.5H_2O$ $(NiCl_2C_{15}H_{14}N_5SO_{0.5})$ M.wt. = 431.97	light green	41.74 (41.66)	2.93 (3.26)	15.99 (16.20)	6.81 (7.40)	56.5	4.15
5	$[Ni(L_2)_2Cl_2]\ 2H_2O$ $(NiCl_2C_{30}H_{30}N_{10}S_2O_2)$ M.wt. = 754.08	light green	47.51 (47.74)	3.92 (4.00)	18.06 (18.56)	7.86 (8.47)	24.4	3.64
6	$[Ni(L_3)_2Cl_2]\ 3.5H_2O$ $(NiCl_2C_{30}H_{33}N_{10}S_2O_{3.5})$ M.wt. = 781.08	light green	45.78 (46.08)	4.16 (4.25)	17.82 (17.92)	7.72 (8.18)	27.8	3.77
7	$[Cu(L_1)Cl_2]\ H_2O$ $(CuCl_2C_{15}H_{15}N_5SO)$ M.wt. = 445.96	green	40.78 (40.36)	2.95 (3.38)	16.31 (15.69)	6.76 (7.13)	56.4	-
8	$[Cu(L_2)_2]\ Cl_2\ 2.5H_2O$ $(CuCl_2C_{30}H_{31}N_{10}S_2O_{2.5})$ M.wt. = 768.07	dirty green	45.98 (46.87)	4.25 (4.06)	17.78 (18.23)	7.98 (8.32)	163.2	1.73
9	$[Cu(L_3)Cl.H_2O]\ Cl\ H_2O$ $(CuCl_2C_{15}H_{17}N_5SO_2)$ M.wt. = 463.97	dark brown	38.64 (38.79)	3.19 (3.69)	15.24 (15.09)	6.49 (6.89)	72.2	1.77
10	$[Cd\ (L_1)Cl_2]\ 0.5H_2O$ $(CdCl_2C_{15}H_{14}N_5SO_{0.5})$ M.wt. = 487.94	white	36.61 (36.89)	2.65 (2.89)	14.44 (14.34)	6.76 (6.55)	10.0	-
11	$Cd\ (L_2)Cl_2]\ 0.5H_2O$ $(CdCl_2C_{15}H_{14}N_5SO_{0.5}\ )$ M.wt. = 487.94	white	36.94 (36.89)	2.35 (2.89)	14.21 (14.34	6.51 (6.55)	22.7	-
12	$[Cd\ (L_3)Cl\ H_2O]\ Cl$ $(CdCl_2C_{15}H_{15}N_5SO)$ M.wt. = 496.94	white	35.99 (36.22)	3.13 (3.04)	14.63 (14.08)	5.96 (6.43)	72.8	-

Molar conductance values of 10^{-3} M DMF solutions are given in (Table 1), their values fall in the range 10.0-56.5 $Ohm^{-1}cm^2\ mol^{-1}$ for all the complexes indicating nonelectrolytic nature of these complexes, except for complexes 2, 3, 9 and 12 are 1:1 electrolytes while the conductivity of the complex 8 is 163.2 $Ohm^{-1}cm^2\ mol^{-1}$ consistent with 1:2 electrolyte [21].

Infrared spectra

Relevant IR bands that can provide structural evidence for the mode of attachment of the ligands to metal ions are reported in (Table 2). The ligands exhibit (thione $\rightleftharpoons$ thiol) tautomerism as given in (Fig. 2). The existence of the thioamide bands in the IR spectra of the free ligands and their complexes indicate that they exist as thione tautomer in the solid state (Fig. 2 (b)) which is in agreement with the previous work on the family of triazole [22-24].

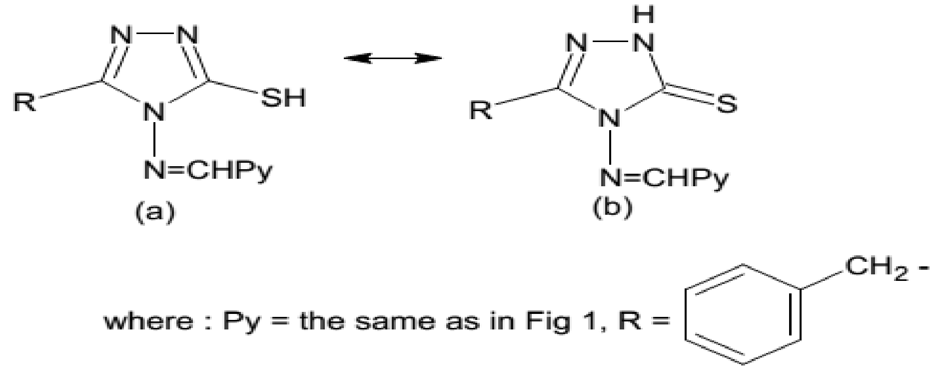


Figure 2: (thione $\rightleftharpoons$ thiol) Tautomeric forms

Table 2. IR spectral data of the free ligands and their metal complexes (cm^{-1})

Compounds				Thioamide			
				I	II	III	IV
	$\nu(H_2O)$	$\nu(NH)$	$\nu(C=N)$	$\delta(C\text{-}H)+\delta(N\text{-}H)$	$\nu(C\text{-}H)+\nu(C\text{-}N)+\delta(C=S)$	$\nu(C\text{-}N)+\nu(C\text{-}S)$	$\nu(C=S)$
L_1	-	3056	1608	1578	1307	1030	802
L_2	-	3056	1615	1581	1286	1008	804
L_3	-	3077	1603	1590	1299	1012	814
$[Cu(L_1)Cl_2]\ H_2O$	3460	3002	1590	1558	1340	1008	795
$[Ni(L_1)Cl_2]\ 0.5H_2O$	3428	3038	1595	1567	1375	1020	781
$[Co(L_1)Cl_2\ H_2O]\ 0.5\ H_2O$	3432	3024	1601	1543	1382	1015	774
$[Cd\ (L_1)Cl_2]\ 0.5H_2O$	3452	3032	1595	1567	1367	1012	790
$[Cu(L_2)_2]\ Cl_2\ 2.5H_2O$	3441	2998	1590	1574	1330	969	745
$[Ni(L_2)_2Cl_2]\ 2H_2O$	3343	3343	1593	1538	1350	970	730
$[Co(L_2)_2Cl(H_2O)]Cl\ 2H_2O$	3351	3042	1593	1507	1354	969	732
$[Cd\ (L_2)Cl_2]\ 0.5H_2O$	3441	3030	1597	1566	1370	992	782
$[Cu(HL_3)H_2OCl]\ Cl\ H_2O$	3448	3033	1577	1542	1333	1005	740
$[Ni(HL_3)_2Cl_2]\ 3.5H_2O$	3407	3028	1596	1572	1335	1001	786
$[Co(L_3)_2Cl\ H_2O]Cl$	3441	3055	1584	1530	1344	1006	732
$[Cd\ (L_3)(\ H_2O)Cl]Cl$	3431	3028	1585	1556	1322	1000	740

The complexing property of RNCS groups with the metal ions has been studied [25]. The free ligands show four bands assignable to the thioamide vibrational frequencies; bands are band-I at 1520–1588 cm^{-1}, band-II at 1300–1400 cm^{-1}, band-III at 1008–1040 cm^{-1} and band IV at 700-850 cm^{-1}. These bands have contributions from δ(C-H) + δ(N-H), υ(C=S) + δ(C-N) + υ(C-H), υ(C-N) + υ(C-S) and υ(C=S) modes of vibration, respectively [25]. These bands are expected to be affected differently by the modes of the coordination to the metal ions. The thioamide IV bands has been found to have maximum υ(C=S) contribution [26]. In the complexes, this band shifts to a lower frequency suggesting the coordination of the sulphur atom in the thione from to metal ions [27]. This also reduces the intensity of the thioamide bands I and II, both with δ(N-H), contributions. Coordination via the sulphur atom shifts the thioamide III band to a lower wavenumbers and reduces its intensity.

The FT-IR spectra of the Schiff bases exhibited a characteristic high intensity band in the region of 1615–1603 cm^{-1} due to ν(C=N) [28]. This band was found to locate at a lower wavenumbers 1601-1577 cm^{-1} in the spectra of complexes indicating that the azomethine nitrogen atom is coordinated to the metal ion.

The new bands in the region of 470 – 462 cm^{-1} in the IR-spectra of the complexes assignable to ν(M–N) stretching frequencies confirm the metal azomethine bonding. The presence of coordination and/or lattice water molecules in the binary complexes is indicated by a broad band within the range 3351–3460 cm^{-1} due to ν(OH) vibrational modes of the water molecules and confirmed by thermal analyses. Also, the rocking mode of coordinated water appears as a weak vibrational band around 700 cm^{-1} and the band observed within the range 600–625 cm^{-1} indicates the presence of lattice water molecules. Thus the IR spectra reflect that the ligands L_1, L_2 and L_3 act as neutral bidentate ligands having coordination sites through thione sulphur and azomethine nitrogen atoms.

Electronic spectra and magnetic studies

The electronic spectra of the Co(II), Ni(II), Cu(II) and Cd(II) complexes have been recorded as DMF solutions in the wavelength range 200-1100 nm. The υ_{max} in kK and ε_{maxin} mol^{-1}cm^2 are depicted in (Table 3). The corrected magnetic moment (μ_{eff}) in Bohr magneton units of the complexes are given in (Table 1).

Table 3: Electronic spectral data for the binary complexes

Complex	υ_{max} (kK)(ϵ_{max} mol^{-1} cm^2)		
	d-d	LMCT	Intraligand
$[Co(L_1)Cl_2(H_2O)_2]$	16.61(372) 15.10(367)	29.79(4130)	37.31(16912)
$[Co(L_2)_2Cl.H_2O]Cl.2H_2O$	16.45(267) 14.92(374)	30.30(6616)	37.31(27506)
$[Co(L_3)_2Cl\ H_2O]Cl$	16.45(248) 14.88(379)	29.41(6490)	37.31(27190)
$[Ni(L_1)Cl_2]0.5H_2O$	15.67(115.5)	29.07(2678)	37.31(17344)
$[Ni(L_2)_2Cl_2]2H_2O$	15.87(768.1) 20.08(1052)	30.30(4411)	37.30(22613)
$[Ni(L_3)_2Cl_2]3.5H_2O$	15.79(169.6) 20.49(406.4)	29.07(4615)	37.17(24640)
$[Cu(L_1)Cl_2]H_2O$	12.12(143)	29.07(1432)	37.36(16500)
$[Cu(L_2)_2]\ Cl_2\ 2.5H_2O$	12.05(116.8)	29.24(2706)	38.02(17700)
$[Cu(L_3)Cl.H_2O]Cl\ H_2O$	11.96(107.9)	28.98(869)	37.53(7781)
$[Cd\ (L_1)Cl_2]0.5H_2O$	-	30.12(4615)	37.31(24640)
$Cd\ (L_2)Cl_2]\ 0.5H_2O$	-	30.03(1997)	37.31(8804)
$[Cd\ (L_3)Cl.H_2O]Cl$	-	29.32(1511)	37.31(7280)

The electronic spectra of Co(II) complexes exhibited absorption bands in the regions of 14.88 – 15.10 and 16.45 – 16.61 kK, corresponding to $^4T_{1g\,(F)} \rightarrow {}^4A_{2g}$ (υ_2) and $^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}$($\upsilon_3$), which indicate the octahedral geometry these complexes. The magnetic moment values of the Co(II) complexes were found in the range 4.3–5.21 B.M, supporting the octahedral geometry for the present Co(II) complexes [29,30].

The Ni(II) complexes 5 and 6 exhibited two bands in the region 15.79-15.87 kK and 20.08–20.49 kK that could be assigned to the transition $^3A_2g \rightarrow {}^3T_1g_{\ (F)}$ and $^3A_2g \rightarrow {}^3T_1g_{\ (P)}$ respectively, and they have magnetic moment values of 3.64 and 3.77 B.M, respectively. These values are generally observed for spin free octahedral geometry Ni(II) complexes [31,32]. The electronic spectrum of Ni(II) complex 4 show one broad absorption d-d band at 15.67 kK which may be attributed to $^3T_{1(F)} \rightarrow {}^3T_{1(P)}$ transitions. This together with the magnetic moment value(4.15 B.M.) suggests a tetrahedral geometry [30]. The electronic spectra of Cu(II) complexes display a broad band around 11.96 – 12.12 kK assignable to $^2B_{1g} \rightarrow {}^2A_{1g}$ transitions [32]. This assignment suggests a square planar geometry for the Cu(II) complexes under investigation. Magnetic moment values are within the range 1.71–1.82 B.M (Table 1). Cd(II) complexes are diamagnetic and colourless as expected for d^{10} system. On the basis of elemental analysis, infrared spectra, molar conductance value and thermal analysis, tetrahedral geometry is suggested for all the Cd(II) complexes.

Thermal analysis

Thermogravimetric analysis (TGA) provides a quantitative measurement of weight change vs temperature, and is typically used to investigate the thermal stability and compositional analysis of complexes. TGA can record directly the weight change as a function of temperature or time for transitions that involve dehydration or decomposition. The presence of coordination and hydration water molecules in the prepared complexes was verified by TGA and reported in (Table 4). The thermal behaviour of the complexes 4, 5, 6, 7, 8, 10 and 11 display a mass loss on the TGA curves of 1.45 – 8.2 % corresponding to loss of 0.5 – 3.5 hydration water molecules (theoretical 1.85 – 8.06 %), within a temperature range of 48 – 205°C. after that, the organic part starts decomposing and it completes at 600°C. The coordination water molecules of the complexes 1, 3 and 12 were lost within a temperature of 197°C as indicated by DTA and TGA curves, with a mass loss of 2.37 – 7.16 % (theoretical 2.44 – 7.84 %). This confirms the results of elemental analysis and reveals that these water molecules are coordinatively bonded to the metal ion in these complexes. However**,** the organic part starts decomposing and it completes at 620°C.

Table 4: Thermal analytical data for binary complexes

	complexes	Temp. range°C	Weight loss %		Loss of moiety	Process
			Calcd.	Found		
1	$[Co(L_1)Cl_2\ (H_2O)_2]$	145	7.84	7.16	$2H_2O$	dehydration
		146-318	16.81	16.58	C_5H_4N	decomposition
		319-437	24.99	25.45	CHN_2;2Cl	decomposition
2	$[Co(L_2)_2Cl\ H_2O]Cl\ 2H_2O$	194	6.98	6.38	$3H_2O$	dehydration
		194-296	26.39	26.64	C_5H_4N; C_7H_7;Cl	decomposition
		296-429	23.41	23.51	C_5H_4N;2CHN;Cl	decomposition
3	$[Co(L_3)_2Cl\ H_2O]Cl$	197	2.44	2.37	H_2O	dehydration
		197-273	17.09	17.9	C_7H_7; Cl	decomposition
		273-324	15.13	14.75	C_5H_4N; Cl	decomposition
4	$[Ni(L_1)Cl_2]\ 0.5H_2O$	177	2.08	2.05	$0.5H_2O$	dehydration
		177-337	24.3	24.1	C_5H_4N; HCN	decomposition
		337-449	16.47	16.26	2Cl	decomposition
5	$[Ni(L_2)_2Cl_2]\ 2H_2O$	185	4.77	4.28	$2H_2O$	dehydration
		186-280	30.1	29.89	$2C_5H_4N$; 2Cl	decomposition
		281-402	31.1	30.13	$2C_7H_7$; 2HCN	decomposition
		403-647	14.05	14.00	2CN; 2HCN	decomposition
6	$[Ni(L_3)_2Cl_2]\ 3.5H_2O$	205	8.06	8.24	$3.5H_2O$	dehydration
		254-375	57.4	56.73	C_5H_4N;2Cl; HCN	decomposition
					C_6H_5N; $2C_7H_7$,	decomposition
		375-651	23.04	23.71	2N;2CN;CHSN; CHN_2	decomposition

7	[Cu(L_1)Cl_2] H_2O	112 258-423 423-651	4.03 25.3 36.2	4.76 25.07 35.58	H_2O C_5H_4N;Cl C_7H_7;HCN_2;Cl	dehydration decomposition decomposition
8	[Cu(L_2)$_2$]Cl_2 2.5H_2O	135 227-284 284-355 355-500	5.85 26.56 28.28 15.62	5.07 26.62 28.25 15.23	2.5H_2O C_5H_4N;Cl;C_7H_7 C_6H_5N;Cl;C_7H_7 2CN;2HCN;N	dehydration decomposition decomposition decomposition
9	[Cu(L_3)Cl H_2O]Cl H_2O	214 229-296 296-352 352-501	7.83 16.94 15.33 25.48	8.33 17.36 15.47 25.21	2H_2O C_5H_4N 2Cl C_7H_7;HCN	dehydration decomposition decomposition decomposition
10	[Cd (L_1)Cl_2] 0.5H_2O	205 230-287 287-399 478-651	1.85 16.02 20.16 18.68	1.45 16.26 20.48 19.11	0.5H_2O C_5H_4N CHN;2Cl C_7H_7	dehydration decomposition decomposition decomposition
11	[Cd (L_2)Cl_2] 0.5H_2O	181 232-305 307-414 416-647	1.85 30.59 24.22 14.98	1.96 30.24 23.73 15.4	0.5H_2O C_5H_4N;2Cl C_7H_7,HCN CSN,NH	dehydration decomposition decomposition decomposition
12	[Cd (L_3)Cl H_2O]Cl	171 173-275 276-397			H_2O C_5H_4N;Cl C_7H_7;Cl	dehydration decomposition decomposition

The thermograms of compounds 2 and 9 (Fig. 3), possess one main stage of decomposition corresponding to loss of both hydration and coordination water molecules in the same stage with a mass loss of (5.07 – 7.16 %) (theoretical 5.85 – 7.84 %) within temperature range (47 – 214°C).

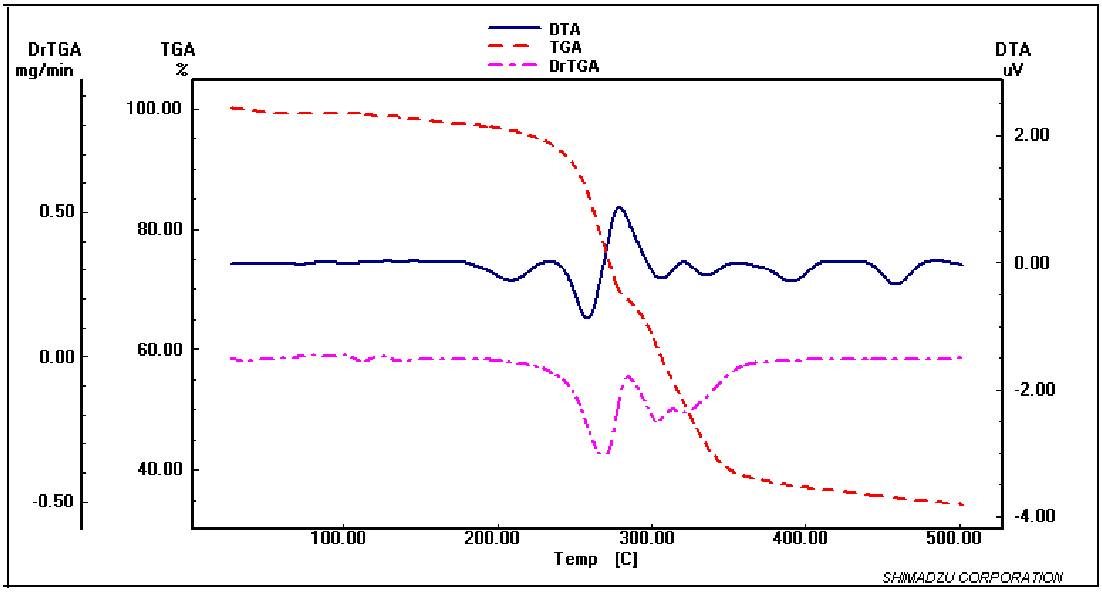
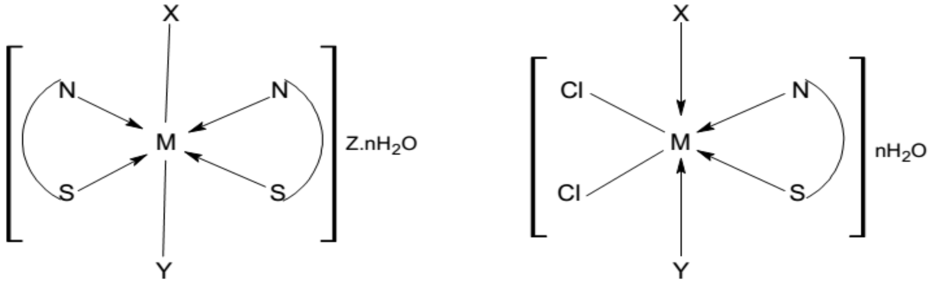


Figure 3: TG-DTG curves of complex 2.

Based on the foregoing data and discussion, the complexes are proposed to have the structures in (Fig. 4).



X=Y=Cl in case complexes 5 and 6; Z=0
X=H_2O, Y=Cl in case complexes 2 and 3;Z=Cl
X=Y = 0 in case complex 8; Z = 2Cl
M = Co(II), Ni(II) and Cu(II)
n = 0 – 3.5

X = Y = H_2O in case complex 1
X =Y = 0 in case complexes 4
7, 10 and 11
M = Co(II), Ni(II), Cu(II) and Cd(II)
n = 0 - 1

Figure 4: Structure of metal complexes N⌒S = L_1, L_2 and L_3.

Antimicrobial activity

All the synthesized Schiff bases and their corresponding Co(II), Ni(II), Cu(II) and Cd(II) complexes were screened *in vitro* for their biological activity by using six bacteria, namely *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Bacillus cereus*, *Micrococcus luteus*, *Escherichia coli and Serratia marcescens* and six fungi, namely *Candida albicans*, *Geotrichum candidum*, *Fusarium oxysporum*, *Scopulariopsis brevicaulis*, *Aspergillus flavus, Trichophyton rubrum* the reported method [20]. The results are systematized in Tables 5 and 6.

Table 5: Antimicrobial activity of ligands and their metal complexes

Compound	Bacteria (Inhibition Zone in mm)					
	Staphylococcus aureus	*Pseudomons aeruginosa*	*Bacillus cereus*	*Micrococcus luteus*	*Escherichia coli*	*Serratia marcescens*
Free L_1	12	1	12	13	11	10
Free L_2	12	10	12	13	13	12
Free L_3	11	10	11	12	11	12
$[Cu(L_1)Cl_2]\ H_2O$	8	8	9	8	8	11
$[Cu(L_2)_2]\ Cl_2\ 2.5H_2O$	9	12	11	10	9	11
$[Cu(L_3)\ Cl.\ H_2O]\ Cl\ H_2O$	9	9	10	10	10	11
$[Ni(L_1)Cl_2]\ 0.5H_2O$	9	10	10	11	10	12
$[Ni(L_2)_2Cl_2]\ 2H_2O$	10	11	12	12	12	12
$[Ni(L_3)_2Cl_2]\ 3.5H_2O$	9	10	11	10	12	13
$[Co(L_1)Cl_2\ (H_2O)_2]$	12	11	11	12	11	12
$[Co(L_2)_2Cl.H_2O]Cl\ 2H_2O$	11	10	10	12	11	12
$[Co(L_3)_2Cl\ H_2O]Cl$	10	9	10	12	10	13
$[Cd\ (L_1)Cl_2]\ 0.5H_2O$	12	13	13	12	13	12
$[Cd\ (L_2)Cl_2]\ 0.5H_2O$	13	11	13	13	12	12
$[Cd\ (L_3)Cl\ H_2O]Cl$	13	11	13	13	13	9

The antibacterial and antifungal studies suggested that all the Schiff bases were found to be biologically active and their metal (II) complexes showed significantly enhanced antibacterial and antifungal activities. In the case of bacteriological studies it was observed that some of the Schiff bases were found potentially active against all bacterial strains. Metal (II) complexes (1-12) of these Schiff bases were also screened against the same bacterial strains. Among these metal complexes compounds 9-12 show higher activity against all bacterial strains. Regarding the antifungal activity, all the Schiff bases showed activity against some fungal species. However, the Co(II), Ni(II), Cu(II) and Cd(II) complexes (1-12) of these Schiff bases showed much enhanced activity as compared to the uncoordinated compounds, All the Schiff bases show good activity against *Candida albicas, Trichophyton rubrum, Geotrichum candidum and Fusarium oxysporum*. Schiff bases and their corresponding Cu(II), Co(II), Ni(II) and Cd(II) complexes are inactive towards *Scopulariopsis brevicaulis and Aspergillus flavus* [33].

Table 6: Antifungal activity of ligands and their metal complexes

Compound	fungal (Inhibition Zone in mm)					
	Candida albicas	*Trichophyton rubrum*	*Geotrichum candidum*	*Fusarium oxysporum*	*Scopulariopsis brevicaulis*	*Aspergillus flavus*
Free L_1	10	10	12	8	-	-
Free L_2	10	9	11	9	-	-
Free L_3	10	8	11	8	-	-
$[Cu(L_1)Cl_2]H_2O$	8	-	12	8	-	-
$[Cu(L_2)_2]\ Cl_2\ 2.5H_2O$	8	-	9	-	-	-
$[Cu(L_3)\ Cl\ H_2O]Cl\ H_2O$	8	-	9	-	-	-
$[Ni(L_1)Cl_2]\ 0.5H_2O$	8	-	9	-	-	-
$[Ni(L_2)_2Cl_2]\ 2H_2O$	8	8	10	8	-	-
$[Ni(L_3)_2Cl_2]\ 3.5H_2O$	8	8	10	8	-	-
$[Co(L_1)Cl_2\ (H_2O)_2]$	10	-	10	8	-	-
$[Co(HL_2)_2Cl.H_2O]Cl\ 2H_2O$	8	8	8	8	-	-
$[Co(L_3)_2Cl\ H_2O]Cl$	10	8	10	8	-	-
$[Cd\ (L_1)Cl_2]\ 0.5H_2O$	8	-	12	-	-	-
$[Cd\ (L_2)Cl_2]\ 0.5H_2O$	11	12	13	9	-	-
$[Cd\ (L_3)Cl.H_2O]Cl$	11	12	14	8	-	9

Conclusion

The synthesized Schiff bases (L_1, L_2 and L_3) act as bidentate ligands and coordinated to the metal ion through the azomethine nitrogen and thione sulphur atoms. The bonding of ligand to metal ion is confirmed by elemental analyses, spectral studies (UV–Vis, FT-IR), TGA, magnetic and conductance measurements. The antimicrobial studies suggested that the Schiff bases were found to be biologically active and their metal complexes showed significantly enhanced antibacterial and antifungal activities against microbial strains in comparison to the free ligands.

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