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Synthesis, magnetic, spectral and antimicrobial activity of new Schiff bases complexes derived from 1,2,4-triazole-5-thione

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Abstract

A series of biologically active new mixed ligand complexes of cobalt(II), nickel(II) copper(II) and cadmium(II) have been synthesized. The reactions of the Schiff base ligand 3-benzyl-1H-4-[(2-methoxybenzylidine)amino]-l,2,4-triazole-5-thione(MBT);3-benzyl-1H-4-[(4- chlorobenzylidine)amino]-1,2,4-triazole-5-thione(CBT); 3-benzyl-1H-4-[(4-nitrobenzylidine)amino]-1,2,4-triazole-5-thione (NBT) and sodium diethyldithiocarbamate trihydrate(dtc) as second ligand. The mixed ligand complexes have been characterized by elemental analyses, spectroscopic measurements (FT-IR, UV-Vis and ESR.), molar conductance, and magnetic measurements. The stoichiometry of these complexes is 1:1:1 ; 1:2:1or 1:1:2 ($M:L_1:L_2$). All mixed ligand complexes have octahedral structures. The free ligands and its their metal complexes were screened for their in vitro antibacterial activity against Gram-negative and Gram-positive bacterial strains and for in vitro antifungal activity. The results of these studies showed that the Cd (II) complexes have higher activity against bacteria and fungi than the free ligands and other metal complexes.

Keywords : coordination chemistry , metal complexes , antibacterial and antifungal activities

1.Introduction

In recent years there has been lots of interest shown in the study of transition metal complexes with substituted 1,2,4-triazoles. Triazoles and their derivatives have proved to be effective pesticides, fungicides and insecticides [1-3] as well as their anti-inflammatory, antimicrobial antitumor, antibacterial, antifungal and antiviral agents [4-10]. The triazole containing ligands used are considered as neutral bidentate ligands and can coordinate to the metal atom through both nitrogen and sulfur atoms and capable of undergoing thione - thiol tautamerism while the Nadtc ligand used behaves as a monobasic bidentate ligand through two sulphur atoms. The present study investigates mixed ligand complexes of Cu(II), Ni(II), Co(II) and Cd(II) with 3-benzyl-1H-4-[(2-methoxybenzylidine)amino]-l,2,4-triazole-5-thione(MBT);3-benzyl-1H-4-[(4- chlorobenzylidine)amino]-1,2,4-triazole-5-thione(CBT); 3-benzyl-1H-4-[(4-nitrobenzylidine)amino]-1,2,4-triazole-5-thione(NBT) (Fig.1). Solid metal complexes were prepared and characterized by elemental analysis, FT-IR, UV-Vis , ESR spectra and magnetic moment determinations. The ligands and its metal complexes showed antibacterial activity against *staphylococcus aureus, pseudomonas aeruginosa, bacillus cereus, micrococcus luteus, escherichia coli and serratia marcescens* and antifungal activity towards the fungi *candida albicans, trichophyton rubrum, geotrichum candidum, fusarium oxysporum, scopulariopsis brevicaulis and aspergillus flavus.*

2. Materials and methods

2.1 .Materials

All chemicals used in the preoperative work were of analytical grade, they include the following: Sodium diethyldithiocarbamate trihydrate, carbon disulphide, potassium hydroxide, absolute ethanol, phenylacetic acid, o-methoxybenzaldehyde, p-nitrobenzaldehyde,p-chlorobenzaldehyde, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $CdCl_2.2.5H_2O$. They were used without further purification.

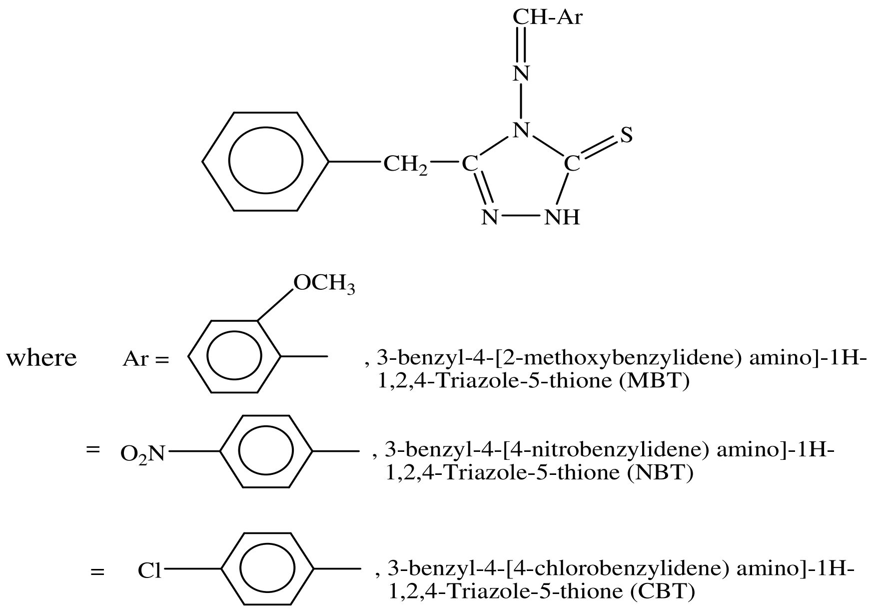

Figure 1: The structure of free ligands

2.2. Synthesis of the mercaptotriazole Schiff bases

The ligands 3-benzyl- 1H -4-[(2-methoxybenzylidine) amino]-l,2,4-triazole-5-thione (MBT), 3-benzyl-lH-4-[(4-chlorobenzylidine)amino]-l,2,4-triazole-5-thione (CBT) and 3- benzyl-1H-4-[(4-nitrobenzylidine)amino]-1,2,4-triazole -5- thione(NBT) were synthesized according to literature survey [11] (Fig. 1). The purity of the ligands was checked *FT*-IR and elemental analysis.

2.3. Synthesis of mixed ligand complexes

To a solution of Cu(II) , Co(II) , Ni(II) and Cd(II) ions (1mmol in 10 mL methanol), a solution of the MBT or CBT or NBT ligands (1 mmol in 25 mL hot methanol) was added drop wise with constant stirring in one direction. When the precipitate was formed, 1 mmol in l0 mL methanol of Nadtc. $3H_2O$ was added. Refluxing of the resulting solution carried for 2-4hours. The product obtained was left overnight, filtered through sintered glass, washed with methanol and dried in vacuum over $CaCl_2$.

2.4. Biological Screening

The antimicrobial activities of the free ligands and its their binary metal complexes were tested against 6 bacterial and 6 fungal strains. All microbial strains were kindly provided by Assiut University Mycological Center (AUMC). These strains are common contaminates of the environment in Egypt and some of which are involved in human and animal diseases (*Trichophyton rubrum, Candida albicans, Geotrichum candidum, Scopulariopsis brevicaulis, Aspergillus flavus)*, plant disease (*Fusarium oxysporum)* or frequently reported from contaminated soil, water and food substances *(Escherichia coli, Bacillus cereus, Pseudomonas aeruginosa, Serratia marcescens, Staphylococcus aureus and Micrococcus luteus).*To prepare inocula for bioassay, bacterial strains were individually cultured for 48h in 100 ml conical flasks containing 30 mL nutrient broth medium. Fungi were grown for 7 days in 100 ml conical containing 30 mL Sabouraud's dextrose broth. Bioassay was done in 10 cm sterile plastic Petri plates in which microbial suspension (1 ml/plate) and 15 ml appropriate agar medium (15 mL /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. The chemical compounds dissolved in dimethyl formamide (DMF) at 2%w/v (=20 mg/mL) were pipette in the 1 /cavity). Cultures were then incubated at 28°C for 48 h in case□cavities (20 of bacteria and up to 7 days in case of fungi. The results were read as the diameter (in mm) of inhibition zone around the cavities. To determine the minimum inhibitory concentrations (MICs), metal complexes, giving positive results were diluted with DMF to prepare a series of descending concentrations down to 0.02 mg/mL. Diluted were similarly assayed as mentioned before and the least concentration (below which no activity) was recorded as the MIC.

2.5. Physical measurements

The carbon, hydrogen, nitrogen and sulfur of the solid mixed ligand complexes were determined by Elementary analyzer system GmbH Varo El. Conductivity measurements for the various mixed ligand complexes were carried out using Jenway 4320 meter lab conductivity meter in DMF solutions at $1x10^{-3}$ M concentrations at room temperature. Electronic spectra of the mixed ligand complexes were run on Perkin Elmer UV/Vis spectrophotometer Lambda 40 using matched silica cells. Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type MSB - Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The calibrate used to be $Hg[Co(SCN)_4]$. The infrared spectra of The free ligands and the prepared mixed ligand complexes were recorded on a Shimadzu 470 infrared spectrophotometer (4000-400cm^{-1}) using KBr discs.

3. Results and discussion

The analytical data of the mixed ligand complexes, including the stoichiometric of the metal mixed ligand complexes as well as their molecular formula, molecular weight, color, effective magnetic moment and molar conductance in dimethyl formamide (DMF) solution are given in Table 1.

Table 1: Analytical and physical data for the mixed ligand metal complexes

No.	Complex [Empirical formula] (formula weight)	Color	Analysis Data				Λ_o Ohm^{-1}cm^2 mol^{-1}	M_{eff} (BM)
			% Found (calculated)					
			C	H	N	S		
1	[Cu(NBT)(dtc)$_2$] $CuC_{26}H_{33}N_7O_2S_5$(699.46)	Brown	44.97 (44.64)	4.56 (4.75)	14.83 (14.01)	22.21 (22.92)	24.60	2.40
2	[Cu(CBT)(dtc)Cl(H$_2$O)] $CuC_{21}H_{25}N_5OS_3Cl_2$(594.10)	Green	42.13 (42.45)	3.73 (4.24)	11.57 (11.78)	16.07 (16.19)	2.57	2.32
3	[Cu(MBT)(dtc)Cl(H$_2$O)] $CuC_{22}H_{28}N_5O_2S_3Cl$(589.68)	Green	44.44 (44.80)	4.19 (4.78)	11.35 (11.87)	16.47 (16.31)	5.88	2.38
4	[Co(NBT)(dtc)Cl(H$_2$O)]0.5H$_2$O $CoC_{21}H_{26}N_6O_{3.5}S_3Cl$(609.05)	Green	41.04 (41.41)	4.24 (4.30)	13.77 (13.79)	15.31 (15.79)	10.15	5.92
5	[Co(CBT)(dtc)Cl(H$_2$O)] $CoC_{21}H_{25}N_5OS_3Cl_2$(589.49)	Brown	42.23 (42.78)	4.72 (4.27)	11.84 (11.88)	16.12 (16.31)	10.69	5.40
6	[Co(MBT)(dtc)Cl(H$_2$O)] $CoC_{22}H_{28}N_5O_2S_3Cl$(585.07)	Dark Brown	45.83 (45.16)	4.40 (4.82)	11.63 (11.97)	16.58 (16.44)	12.64	5.21
7	[Ni(NBT)(dtc)Cl(H$_2$O)]0.5H$_2$O $NiC_{21}H_{26}N_6O_{3.5}S_3Cl$(609.05)	Green	41.75 (41.42)	4.90 (4.30)	13.87 (13.80)	15.09 (15.80)	11.37	3.25
8	[Ni(CBT)$_2$(dtc)]Cl $NiC_{37}H_{36}N_9S_4Cl_3$(900.05)	Green	49.47 (49.37)	4.28 (4.03)	13.90 (14.00)	14.15 (14.25)	69.13	3.35
9	[Ni(MBT)(dtc)$_2$(H$_2$O)].2H$_2$O $NiC_{27}H_{40}N_6O_3S_5$(715.66)	Green	45.93 (45.31)	5.30 (5.63)	11.92 (11.74)	22.84 (22.40)	5.10	3.64
10	[Cd(NBT)(dtc)]Cl.H$_2$O $CdC_{21}H_{25}N_6O_3S_3Cl$(653.52)	White	38.29 (38.59)	3.96 (3.85)	12.51 (12.85)	17.92 (17.71)	69.90	-
11	[Cd(CBT)(dtc)]Cl.H$_2$O $CdC_{21}H_{25}N_5OS_3Cl_2$(642.97)	White	39.44 (39.22)	3.77 (3.91)	10.66 (10.89)	15.03 (14.96)	85.64	-
12	[Cd(MBT)(dtc)]Cl $CdC_{22}H_{26}N_5OS_3Cl$(620.53)	White	42.08 (42.58)	3.96 (4.22)	11.70 (11.28)	15.33 (15.50)	83.23	-

The data clearly indicate that the free ligands used act as neutral bidentate ligands while Nadtc.3H$_2$O ligand acts as a monobasic bidentate ligand. The methods used for the preparation and isolation of the mixed ligand complexes give materials of good purity as supported by their analyses. All the mixed ligand complexes are colored except Cd(II) complexes. They are stable in air and non-hygroscopic. The synthesized mixed ligand complexes are sparingly soluble in the common organic solvents, but they are completely soluble in DMF or DMSO. The molar conductance values for the mixed ligand complex which indicates the non-electrolyte nature of these complexes except the mixed ligand complexes (8) and 10-12 show molar conductance values within the values in the range 69.13-85.64 Ohm^{-1} cm^2 mol^{-1} indicating that these complexes are 1:1 electrolytes [12].

3.1. UV-Visible spectra and magnetic susceptibility measurements

The electronic spectra of the mixed ligand complexes have been recorded as DMF solutions. The obtained spectral characteristic data (mainly υ_{max} in kK and ε_{max} in cm^2mol^{-1}) of the mixed ligand complexes are given in Table 2.

Table 2: Electronic spectral data (υ_{max} in kK, ε_{max} in $mol^{-1}cm^2$) of the metal complexes in DMF solutions.

No.	Complex	υ(kK) (ε_{max} in cm^2 mol^{-1})	Assignment
1	$[Cu(NBT)(dtc)_2]$	33.91(52140.36) 16.96(191.64)	Intraligand d-d
2	$[Cu(CBT)(dtc)Cl(H_2O)]$	36.90(2489.46) 23.52(995.08) 16.91(73.18)	Intraligand LMCT d-d
3	$[Cu(MBT)(dtc)Cl(H_2O)]$	36.52(28100.51) 22.83(5940.56) 16.07(297.10)	Intraligand LMCT d-d
4	$[Co(NBT)(dtc)Cl(H_2O)]0.5H_2O$	34.73(57400.25) 17.09(244.10)	Intraligand d-d
5	$[Co(CBT)(dtc)Cl(H_2O)]$	35.86(61351.04) 15.26(67.66)	Intraligand d-d
6	$[Co(MBT)(dtc)Cl(H_2O)]$	36.64(48445.26) 30.94(33192.60) 20.00(353.90) 15.29(167.70)	Intraligand Intraligand LMCT d-d
7	$[Ni(NBT)(dtc)Cl(H_2O)]0.5H_2O$	37.37(22508.34) 30.94(78320.51) 25.42(1042.43) 23.69(6120.58) 15.87(68.70)	Intraligand Intraligand LMCT LMCT d-d
8	$[Ni(CBT)_2(dtc)]Cl$	36.27(21432.05) 30.67(83746.61) 25.94(13240.57) 23.60(3412.70) 21.10(338.00) 15.79(120.90)	Intraligand Intraligand LMCT LMCT LMCT d-d
9	$[Ni(MBT)(dtc)_2(H_2O)].2H_2O$	37.00(38410.61) 30.65(61242.62) 25.95(12480.14) 23.64(2514.10) 20.74(170.94) 15.75(61.98)	Intraligand Intraligand LMCT LMCT LMCT d-d
10	$[Cd(NBT)(dtc)]Cl.H_2O$	36.87(25404.05) 35.18(26895.14) 30.07(1739.24)	Intraligand Intraligand Intraligand
11	$[Cd(CBT)(dtc)]Cl.H_2O$	37.26(37160.16) 35.26(31532.07) 29.27(2801.00)	Intraligand Intraligand LMCT
12	$[Cd(MBT)(dtc)]Cl$	37.28(49920.04) 35.26(40982.67) 30.65(16247.96)	Intraligand Intraligand Intraligand

The corrected magnetic moment ($\mu_e$ff) in Bohr monitoring units of the mixed ligand complexes is given in Table *1*. Three sets of bands could be recognized in the electronic spectra of the obtained mixed ligand complexes. The first set of bands with υ_{max} in the range 30.07 - 37.37 kK., could be attributed to Intraligand charge transfer transitions [13]. The second set includes bands having υ_{max} in the range 20.00-29.27 kK. These bands are assigned to be L→MCT transitions [14]. The third set of bands of Cu (II) mixed ligand complexes was found to have υ_{max} within the range 16.07 - 16.95 kK. This band is due to a d-d transition and it is typical for tetragonal distorted octahedral Cu (II) mixed ligand complexes. This band could be assigned to include all the three transitions $^{2}B_{1g}\rightarrow{}^{2}B_{2g}$, $^{2}Bi_{g}\rightarrow{}^{2}A_{1g}$ and $^{2}B_{1g}\rightarrow{}^{2}E_{g}$ [14]. The magnetic moment values for Cu(II) mixed ligand complexes at room temperature were found to be within the range 2.32 and 2.40 B.M. These values are typical with those expected for spin free octahedral Cu (II) complexes [15].

Co (II) mixed ligand complexes displays d-d transition bands covering the υ_{max} range 15.26- 17.09 kK. These bands could be attributed to $^{4}T_{1g}(F)\rightarrow{}^{4}A_{2}g(\upsilon_{2})$ and $T_{1g}(F)\rightarrow{}^{4}T_{1}g(P)(\upsilon_{3})$ transitions. The position of the d-d bands of the Co (II) mixed ligand complexes is indicative of a distorted octahedral geometry [16].

The higher magnetic moment values (5.21and 5.4 B.M.) of the complexes (5and 6) may be attributed to the presence of the lower symmetry component in the ligand field as well as the covalent nature of the metal ligand bonds [16]. The d-d band of Ni (II) complexes was found to have υ_{max} in the range 17.57- 17.87 kK. This band could be assigned to $^{3}A_{2g}(F)\rightarrow{}^{3}T_{1g}(F)$ transitions suggesting octahedral geometry [14]. On the other hand, The room temperature magnetic moment values for Ni(II) mixed ligand complexes are 3.25, 3.35 and 3.64 B.M suggesting an octahedral structure for these complexes [14].

3.2. FT-IR Spectra

The assignment of the FT-IR bands of all the mixed ligand complexes will be as shown in Table 3. The free mercaptotriazole Schiff base ligands show four bands at 1588-1540, 1282-1340, 1008-1040 and 780-814 cm^{-1} which are assignable to thioamide I, II, III and IV vibrations, respectively. In the complexes, these bands suffer a shift, suggesting the coordination of the sulfur atom to the metal ions [16]. All these ligands and their complexes show a band at within the range 3102-3030 cm^{-1} attributed to υ(NH) vibration, indicating that the free ligands and their complexes are in the thione form. The strongest bands observed in the range 1619-1625 cm^{-1} in the IR spectra of NBT, CBT and MBT ligands can be assigned to υ(C=N) vibrations of the azomethine group. This band in the complexes shifted to lower frequency indicating the coordination of the azomethine nitrogen to the metal ions. The bands observed in the region 480-520 cm^{-1} may be assigned to υ(M-N) vibration[17].

The IR spectrum of the free dtc ligand displayed two bands at 982 and 628 cm^{-1} due to $\upsilon_{asym.}$(C-S) and $\upsilon_{sym.}$(C-S) vibrations, respectively. These bands are suffering a shift to higher frequencies. This indicates the symmetrically bidentate nature of the dithiocarbamate ligand [18].

On studying the IR spectrum of the dithiocarbamate (Nadtc) ligand, a characteristic band of the thioureide [NCS_2] group obtained at 1474 cm^{-1}, the band defines a carbon nitrogen bond in order to be intermediate between single C-N bond and double C=N bond [19]. The appearance of an IR signal in that region in the spectrum of the free dithiocarbamate (Nadtc) ligand indicates that amongst the four possible resonance structures (Figure 2), in our case we are dealing with a considerable contribution of structure (I), characterized by a strong delocalization of electrons in the dithiocarbamate moiety. The assignment of FT-IR bands too υ(C=S) [$\upsilon_{asym.}$(C-S) and $\upsilon_{sym.}$(C-S)] vibrations in the dithiocarbamate moiety[19,20] follows. The IR spectrum of the free dtc ligand displayed two bands at 982 and 628 cm^{-1} due to $\upsilon_{asym.}$(C-S) and $\upsilon_{sym.}$(C-S) vibrations, respectively. These bands are suffered a shift to higher frequencies. This indicates the symmetrically bidentate nature of the dithiocarbamate ligand [20].

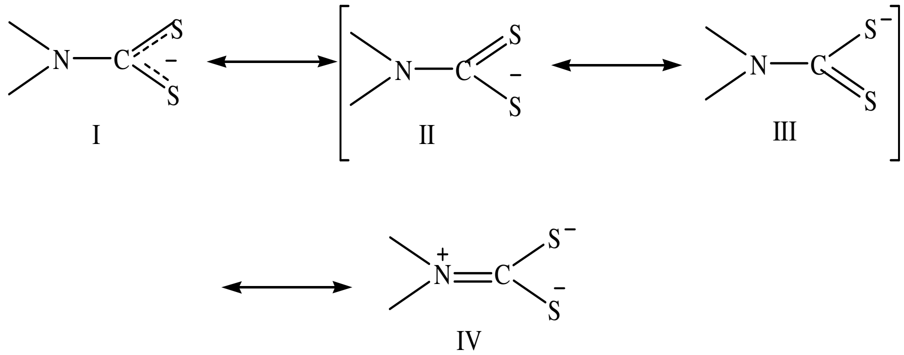

Figure 2: Resonant forms of the dithiocarbammic NCSS' moiety

On studying the IR spectrum of the dithiocarbamate (Nadtc) ligand, a characteristic band of the thioureide [NCS_2] group obtained at 1474 cm^{-1}, the band defines a carbon nitrogen bond in order to be intermediate between single C-N bond and double C=N bond [19]. The appearance of an IR signal in that region in the spectrum of the free dithiocarbamate Nadtc) ligand indicates that amongst the four possible resonance structures (Figure 2), in our case we are dealing with a considerable contribution of structure (I), characterized by a strong delocalization of electrons in the dithiocarbamate moiety.

Table 3: Relevant FT-IR spectral data (cm^{-1}) for the mixed ligand metal complexes

Complex	υ (O-H)(H_2O)	Thioamide Bands				Dtc characteristic bands			
		I δ(C-H)+δ(N-H)	II υ(C=S)+υ(C-N)+δ(C-H)	III υ(C-N)+υ(C-S)	IV υ(C=S)	υ(C-N) [NCS_2]$^-$	υ (N-C)(CNC)	υ (C=S)	
								$υ_{asym.}$ (C-S)	$υ_{sym.}$ (C-S)
1	-	1585	1360	1025	840	1490	1155	1010	680
2	3380	1580	1290	1050	810	1480	1150	995	690
3	3400	1590	1320	1080	830	1500	1160	1000	680
4	3420	1590	1340	1030	845	1490	1170	1010	690
5	3400	1590	1360	1030	855	1520	1175	1020	665
6	3450	1595	1350	1060	845	1495	1170	990	630
7	3450	1580	1300	1050	840	1490	1150	995	660
8	-	1590	1295	1070	840	1515	1140	990	670
9	3350	1590	1310	1070	830	1510	1150	995	650
10	3300	1580	1345	1025	840	1490	1140	990	695
11	3350	1590	1340	1030	830	1490	1170	995	710
12	-	1590	1380	1050	850	1505	1170	1010	695

Passing from the free dithiocarbamate (Nadtc) ligand to its mixed ligand complexes, then υ(C-N) mode of the thioureide [NCS_2] group[20] is shifted to higher frequency regions; this is attributed to mesmeric drift of the electron density from the dithiocarbamate moiety towards the metal ions [19].The presence of coordination and lattice water molecules in the prepared mixed ligand complexes containing water molecules is indicated by a broad band within the range 3326- 3459 cm^{-1} due to υ (OH) vibration modes of the water molecules and confirmed by thermal analysis. Also, the rocking mode of coordinated water appeared as a week vibration band around 700 cm^{-1} and the band observed within the range 600-625 cm^{-1} indicates the presence of lattice water molecules [20].

3.3. ESR Studies of Cu(II) complexes

X-band ESR spectra of Cu(II) complexes were recorded in solid state at 25°C gave a abroad line centered on g = 2.1, 1.03 and without resolved for Cu(II) can be attributed to the dipolar effect caused by mutual interactions between . Nuclear spin of the (C=N) (I=L) with the unpaired of electron density of Cu(II) [21] . The spin Hamiltonian parameters for [Cu(II)-Oct.] (S = 1/2, I =7/2) hyperfine structure were calculated. The g-tensor values can be used to derive the ground state. The absence of copper hyperfine coupling in common in the solid state and is attributed to the simultaneous flipping of neighboring electron spin [20] or strong exchange interactions which average out the interaction with the nuclei. For octahedral complex the shape of the spectrum, spectral studies and magnetic moment (μ =2.32- 2.40 B. M.) agrees with proposed structures. For elemental analysis, FT-IR, electronic spectra, molar conductance, magnetic moment , and ESR spectra tentative structures of the metal complexes are proved in Fig. 3.

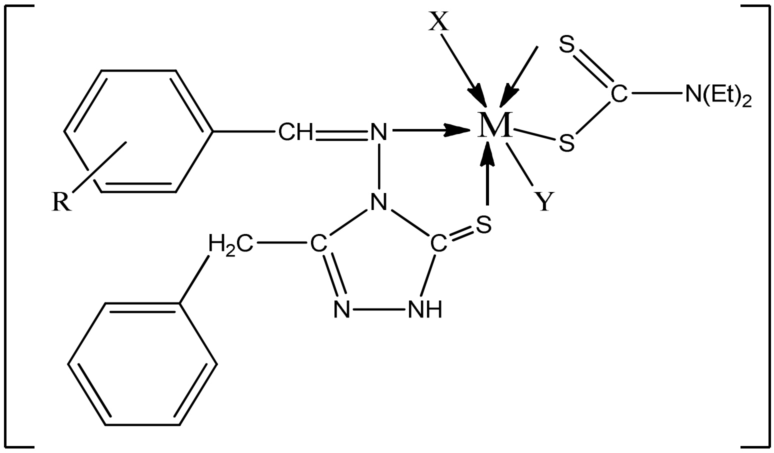

Figure 3: Proposed structure of (1:1:1) metal complexes
Where : M= Cu(II), Co(II), Ni(II) or Cd(II) ; R = 2-OCH_3; 4-NO_2 or 4-Cl

3.4. Antibacterial activity

Antibacterial activities of the free ligands and its complexes were tested against the bacterial like *Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus cereus, Micrococcus luteus, Escherichia coli and Serratia marcescens*. Moreover, these compounds also the antifungal activity against like Candida albicans, Trichophyton rubrum, Geotrichum candidum, Fusarium oxysporum, Scopulariopsis brevicaulis and Aspergillus flavus. The biological activity of the complexes was listed in Table 4 and 5 and their the results were compared with the free ligands and its metal complexes. The above values clearly indicate that the zone of inhibition area is greater for the metal complexes than the free ligands. The increase in antibacterial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and the ligand. Such increased activity of the metal chelates could be explained on the basis of Overton's concept and chelating theory. The free ligand L_2 and its complexes exhibited higher activities than L_1 or L_3 and its complexes, because of electron donating group nature of the methoxy group in the ligand environment. The Cd(II) complexes also showed higher antibacterial effects than those of the Cu(II) , Ni (II) and Co(II) complexes. This phenomenon was explained based on chelating theory. Thus Ni (II) chelate no showed antifungal activity towards *Trichophyton rubrum and Fusarium oxysporum.* However, the free ligands and its metal chelate showed no antifungal activity on *Scopulariopsis brevicaulis and Aspergillus flavus.* The antibacterial and antifungal activity of the complexes increased in the order: Cd(II) > Cu(II) > Ni(II) > Co(II).

Table 4: Antimicrobial activity of free ligands and its metal complexes

NO.	Compound	Bacteria (Inhibition zone in mm)					
		Staphylococcus aureus	*Pseudomonas aeruginosa*	*Bacillus cereus*	*Micrococcus luteus*	*Escherichia coli*	*Serratia Marcescens*
1	Free L_1	12	12	11	13	11	11
2	Free L_1	14	14	15	15	13	14
3	Free L_1	11	10	10	12	10	10
4	Ni(II)-L_1	13	14	13	15	13	13
5	Ni(II)-L_2	15	16	16	17	15	16
6	Ni(II)-L_3	12	12	11	14	13	12
7	Co(II)- L_1	12	13	12	14	12	12
8	Co(II)- L_2	14	15	15	15	14	14
9	Co(II)- L_3	12	11	11	13	11	11
10	Cu(II)- L_1	14	15	14	16	15	14
11	Cu(II)- L_2	16	17	17	18	17	18
12	Cu(II)- L_3	13	13	12	15	14	13
13	Cd(II)- L_1	16	18	16	19	17	17
14	Cd(II)- L_2	18	19	19	20	17	19
15	Cd(II)- L_3	16	14	15	17	17	15

Table 5: Antifungal activity of free ligands and its metal complexes

NO.	Compound	Fungal (Inhibition zone in mm)					
		Candida albicans	*Trichophyton rubrum*	*Geotrichum candidum*	*Fusarium oxysporum*	*Scop ulariopsi sbrevicaulis*	*Aspergillus flavus*
1	Free L_1	10	7	10	8	-	-
2	Free L_1	11	9	11	9	-	-
3	Free L_1	10	8	11	8	-	-
4	Ni(II)-L_1	12	-	14	-	-	-
5	Ni(II)-L_2	13	-	16	-	-	-
6	Ni(II)-L_3	11	-	13	-	-	-
7	Co(II)- L_1	11	13	13	12	-	-
8	Co(II)- L_2	12	14	15	13	-	-
9	Co(II)- L_3	11	12	12	12	-	-
10	Cu(II)- L_1	13	14	16	14	-	-
11	Cu(II)- L_2	14	15	17	16	-	-
12	Cu(II)- L_3	12	12	14	12	-	-
13	Cd(II)- L_1	15	17	17	16	-	-
14	Cd(II)- L_2	16	18	18	16		
15	Cd(II)- L_3	14	15	15	14	-	-

Conclusion

1. The mixed ligand complexes of Cu(II), Co(II) , Ni(II) and Cd(II) have been characterized by elemental analyses, spectroscopic measurements (FT-IR, UV-Vis and ESR.), molar conductance, and magnetic measurements.
2. The Stoichiometric of these complexes is 1:1:1 ; 1:2:1or 1:1:2 (M:L_1:L_2). Cu(II), Co(II) , Ni(II) and Cd(II) mixed ligand complexes showed octahedral structures.
3. The synthesized ligands and its metal complexes were screened for their in vitro antibacterial activity against Gram-negative and Gram-positive bacterial strains and for in vitro antifungal activity.
4. The results of these studies showed that the Cd(II) complexes have highest antibacterial and antifungal activities than the free ligands and other metal complexes.

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