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Preparation and Biological Study of *1,2,4-Iso*proplydine Malonate Bisriazoles and Bisisatin Transition Metal Complexes

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ABSTRACT

Three ligands were synthesized from the reactions of isopropylidene diethyl malonate or diethyl malonate hydrazides to form two heterocyclic rings of 1,2,4-triazoles [L_1, 5,5'-(2-methylprop-1-ene-1,1-diyl)bis(4-phenyl-2,4-dihydro-3H-1,2,4-triazole-3-thione)], [L_2, 5,5'-(2-methylprop-1-ene-1,1-diyl)bis(2,4-dihydro-3H-1,2,4-triazole-3-thione)], and isatine Schiff base [L_3, N'1,N'3-bis[(3E)-2-oxo-1,2-dihydro-3H-indol-3-ylidene]propanedihydrazide]. These ligands were characterized and studied by the following techniques: UV-visible, FT-IR spectroscopy, ^1H and ^{13}C NMR spectroscopy, elemental analysis (C.H.N). These ligands coordinate to following metal ions; Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2}, and their complexes were studied by magnetic susceptibility, molar conductivity, atomic absorption and molar ratio method. From these measurements may suggest the following configuration for these complexes: (a) octahedral geometry for the formula: $[M(L_1)(H_2O)Cl]Cl$ ($M = Cr^{+3}$), and $[M(L_1)(H_2O)]$ ($M = Mn^{+2}, Ni^{+2}$), (b) octahedral geometry with dimmer structure for the formula: $[M_2(L^*)_2(H_2O)_4Cl_2]\ Cl_2$ (where $L^* = L_1, L_2$. $M = Co^{+2}, Cu^{+2}$), and (c) octahedral geometry of the formula $[M(L_3)]Cl_2$ ($M = Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}$ and Cu^{+2}). The bactericidal activity of these complexes were determined for four local strains of pathogenic bacteria: Escherichia Coli, Staphylococcus aureus, Proteus mirabilis, and Pseudomonas aeruginosa, and some of these compounds exhibit the effectiveness of anti-Microbial activity.

Keywords: *1,2,4-Iso*proplydine malonate bisriazoles, *bis*isatin, Schiff base, biological Study and transition metal complexes.

INTRODUCTION

The 1,2,4-Triazole represent a class of five-membered heterocyclic compounds of great importance for the preparation of new drugs with diverse biological activities because they may present several structural variations with the same numbers of carbon and nitrogen atoms. Many 1,2,4-Triazole and their derivatives are found to be associated with various biological activities such as antibacterial [1-4], antifungal [5], analgesic [6], anticancer [7-8], antiviral [9], antitubercular [10,11], anti-inflammatory [12], and anticonvulsant [13,14], antidepressant [15], and central nervous system (CNS) [16]. Several compounds containing 1,2,4-triazole rings are well known as drugs. For example, fluconazole can be used in the treatment and prevention of superficial and systemic fungal infections, which is synthesized from a halogenated acetophenone derivative [17], while vorozole, letrozole [18] and anastrozole [19] are non-steroidal drugs used for the treatment of cancer [20] and loreclezole is used as an anticonvulsant [21]**.**

The 1,2,4-triazole ligands show a great coordination diversity, especially when the triazole nucleus is substituted with additional donor groups. This property together with their strong (*s*) donor properties and the relative ease of synthesis make them very appealing for the design of new polynuclear metal complexes with interesting properties. The use of triazole and triazolate based ligands in conjunction with iron(II) is of considerable interest because of the possibility of generating magnetically interesting complexes, specifically complexes that exhibit spin crossover (SCO). The first dinuclear iron(II) complexes of any 4-substituted 3,5-di(2-pyridyl)-4H-1,2,4-triazole ligands, $[Fe^{II}_2(adpt)_2(H_2O)1.5\text{-}(CH_3CN)2.5](BF_4)_4$ and $[Fe^{II}_2(pldpt)_2(H_2O)_2(CH_3CN)_2](BF_4)_4$, are presented [where adpt is 4-amino-3,5-di(2-pyridyl)-4H-1,2,4-triazole and pldpt is 4-pyrrolyl-3,5-di(2-pyridyl)-4H-1,2,4-triazole] [22-23].Gusev *et al* describe the synthesis of many bistriazole ligands two heteroleptic dibenzoylmethanate europium(III) complexes with 1,3-bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)propane (H_2L_1) and 1,4-bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)butane (H_2L_2) and they found that they possess photo- and electroluminescent properties[24]. Neutral Pt(II) complexes bearing tridentate dianionic 2,6-bis(1 H -1,2,4-tria zol-5-yl)pyridine and ancillary alkyl-substituted pyridine ligands have been synthesized and characterized by Mydlak *et al*. They show bright green emission, reaching 73 % photoluminescence quantum yield in deareated chloroform solution, which can be assigned to a predominantly metal-perturbed ligand -centered phosphorescence [25]. A series of new 1,2/1,3-bis[o-(N-methylidenamino-3-aryl-5-phenyl-4H-1,2,4-triazole-4-yl)phenoxy] ethane/propane derivatives were prepared in good yields by treatment of 4-amino-3-aryl-5-phenyl-4H-1,2,4-triazoles with certain bis-aldehydes. They are expected to exhibit some biological activities and these results will be reported in due course [26]. New bistriazole-Schiff base, were synthesized and characterized. Remarkable complexation properties are found towards some transition metal cations. The ion binding properties were examined by using it in solvent extraction for Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Fe^{3+}, Cd^{2+}, Ca^{2+}, Mg^{2+} and Zn^{2+} ions from aqueous solutions into the organic phase. The stability sequences of the triazole derivatives in $CHCl_3$ for the metal cations generally found in order: Fe(III) > Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II) > Ni(II) > Mg(II) > Ca(II). The synthesized compounds were tested for antimicrobial activity using the agar diffusion technique against 11 bacteria [27].

The aim of this study is to prepare new multidentate ligands containing two nucleus of 1,2,4-triazoles on malonate skeleton and to characterize the products and to study the molecularity of coordination with some first row transition metals. It also aimed to check biological activities of their metal complexes as bactriocides.

MATERIALS AND METHODS

Materials and Instrument: All chemicals used were of analytical reagent grade, or of the highest purity available. Diethyl malonate, phenyl isothiocyanate, and all metal chlorides obtained from BDH, England. Hydrazine hydrate, sodium hydroxide, ammonium acetate were obtained from Thomas, India. Micro-analysis (C.H.N) has been performed by using EuroEA3000 Series (CHNS) Elemental Analyzer. Melting points were recorded using Stuart Scientific melting point SMP without correction. Electronic spectra were recorded using Varian Cary 100 conc. spectrophotometer (200 - 900 nm). FT-IR spectra of starting materials used for and ligands were recorded as KBr discs in the region (400 - 4000 cm^{-1}) on Shimadzu FT-IR 8400S spectrophotometer. Molar conductivities of the prepared complexes were measured in dimethylsulphoxides (DMSO) solution ($\sim 2 \times 10^{-3}$ M) by using (WTW740) supplied with 1 cm platinum cell. The magnetic susceptibility measurements were made at room temperature using Magnetic Susceptibility Balance Model (MSB-MKI) following Faraday method. The metal contents of the complexes were determined by atomic absorption (A.A) technique, using a Shimadzu (AA680) atomic absorption spectrophotometer. ^1H and ^{13}C NMR spectra were recorded using Ultra Shield 300 MHz, Bruker, Switzerland, by using DMSO as solvent and TMS as reference.

Preparation of Ligands

(a) Preparation of isopropylidenemalonate dihydrazide (M_1): A mixture of diethylisopropylidene malonate (20.02 g, 0.10 mol) and hydrazine hydrate (80 %) (11.0 g, 0.22 mol) in absolute ethanol (25 mL) was refluxed for 1 hours. The reaction mixture cooled and the formed precipitate was filtered, and then washed with water. The crude *iso*propylidenemalonate dihydrazide was recrystallized from ethanol to give yellow crystal of the sought product, dried at 60^0C for five hours.

(b) Preparation of isopropylidenemalonylbis(phenylhydrazine-carbothio-amide) (M_2): A mixture of *Iso*propylidenemalonate dihydrazide (3.5 g, 20.0 mmol), which prepared following previous procedure, and the phenyl isothiocyanate (5.4g, 40.0 mmol) in absolute ethanol (25 mL) was refluxed for 1 h. A precipitate formed after half an hour, and the reflux was continued for further hour. The precipitate was cooled to room temperature and was filtered. The precipitated powder was recrystallized from ethanol-water, dried at 60^0C for five hours.

(c) Preparation of isopropylidenemalonyl bis(hydrazine carbothio-amide) (M_3):A mixture of *iso*propylidenemalonate dihydrazide (20.0 g, 80.0 mmol) solution in concentrated hydrochloric acid (10 mL), and potassium thiocyanate (0.2 mol, 19 g) for three hours. The mixture cooled to ambient temperature, and neutralized with saturated solution of potassium hydrogen carbonate ($KHCO_3$). A precipitate was filtered on filter paper and was washed with distilled water. The precipitate was recrystallized from ethanol, to give colorless powder.

(d) Preparation of 5,5'-(2-methylprop-1-ene-1,1-diyl)bis(4-phenyl-2,4-dihydro-3H-1,2,4-triazole-3-thione)(L_1): A mixture of *iso*propylidene malonyl *bis*(phenyl-hydrazinecarbothioamide) (M_2) (4.52 g, 10.0 mmol) and 2N NaOH solution (10.0 mL) refluxed for three hours. The reaction mixture was neutralized with concentrated hydrochloric acid solution, and white precipitate was formed. The precipitate was filtered, washed with three portions of water (5.0 mL), and then recrystallized from ethanol-water to give nice needles of title compound.

(e) Preparation of 5,5'-(2-methylprop-1-ene-1,1-diyl)bis(2,4-dihydro -3H-1,2,4-triazole-3-thione) (L_2):A mixture of *iso*propylidenemalonyl*bis*-(hydrazine carbothioamide) (3.0 g, 10.0 mmol) in ethanol (15 mL), and aqueous solution of 2N sodium hydroxide (10 mL) was refluxed for ten hours on a steam bath. The mixture cooled to ambient temperature and acidified with dilute hydrochloric acid to adjust the pH in range 5.0 - 6.0. The white crud precipitate was filtered, washed with two portions of cold distilled (5 mL). The crude precipitate recrystallized from 1:2 ethanol:methanol mixture, to give white crystals of the title compound.

(f) PreparationofN'1,N'3-bis[(3E)-2-oxo-1,2-dihydro-3H-indol-3-lidene]propane-dihydrazide (L_3): A solution of Malonic Dihydrazide (13.2 g, 10.0 mmol) in 25 mL of ethanol and isatin (2.94 g, 20.0 mmole) was refluxed for 1 h. The mixture cooled to room temperature, and the residue was filtered on filter paper. The crude residue recrystallized from a mixture of dichloromethane:ethanol and dried at 80^0C for 5 hours.

Preparation of metal complexes

(a) The metal complexes of the ligands L_1, and L_2 were prepared for the metal ions: manganese, chromium, iron, cobalt, nickel, chromium and copper by following the general procedure below: An equivalent of the ligand (5.0 mmole) was dissolved in ethanol (50 mL), with aid of gentle heating until a clear solution was obtained. A solution of the metal chloride in minimum amount of ethanol was slowly added with efficient stirring. The mixture was refluxed for 1 hour, and the precipitate formed was filtered by filter paper. The precipitate was washed with five portions of a mixture of 1:1 ethanol: distilled water (5.0 mL), then with two portion of diethyl ether (5.0 mL). The product was dried at 60^0 C for 5 h.

(b) Similar procedure was followed for (L_3) complexes, except that drops ammonia/ammonium acetate solution (pH = 8.0) was added to bring the reaction pH above 7.0.

Determination of Complexes stoichiometry: The complexes stoichiometry (molecularity) of new complexes were measured by following the same procedure (Molar ration method) mentioned by Srilalitha *et al*. [28]**.** The method based on measuring the absorbance of a set of mixture of maney dilutions of ligand solution and keeping the metal concentration constant under optimal conditions. The molar ratio of M/L ratio was calculated by plotting the absorbance of these mixtures at λ_{max} against it's the molar ratio.

Biological Activity: The bactericidal activity of these complexes were determined for four local strains of pathogenic bacteria: Escherichia Coli, Staphylococcus aureus, Proteus mirabilis, and Pseudomonas aeruginosa, following Well-diffusion agar method mentioned in literature [29]. Eight holes of 6 mm diameter was made in the agar of a disposable plastic Petri plates, and 50 µl aliquot of 1.0, 2.0, 3.0, 4.0, and 5.0 ppm metal complexes solutions to be tested, were placed.

RESULTS AND DISCUSSION

Bistriazole and bisisatin ligands were prepared by refluxing one mole of diethylisopropylidene malonic dihydrazides and two mole of phenyl isothiocyanate potassium thiocyanate in ethanol, or diethyl malonic dihydrazides with isatin as shown in figs. 1 and 2. Further treatment of the first two product with hot alkli result in forming 1,2,4-bistiazoles ligands (L_1 and L_2). The structure of the synthesized compounds (M_1, M_2, M_3, L_1, L_2, and L_3) has been characterized by U.V., FT-IR, ^{1}H-NMR and ^{13}C-NMR spectrum, and elemental analysis. The data of these measurements were presented in tables 1 - 3, and their results are in good agreement with expected products structure.

Table 1: Physical properties for prepared compounds and ligands.

Comp.	Structure	Mol. Wt	M.p ^{0}C	λ (nm)	Color	Yield %	C %		H %		N %		S %	
							Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.
M_1	$C_6H_{12}N_4O_2$	172	102-104	225	Faint yellow	64	41.85	41.52	7.02	7.24	32.54	33.08	-	-
M_2	$C_{20}H_{22}N_6O_2S_2$	442	150-152	268	White	92	54.28	54.83	5.01	5.68	18.99	19.12	14.49	13.87
M_3	$C_8H_{14}N_6O_2S_2$	290	76-78	254	White	76	33.09	34.14	4.86	5.08	28.94	29.20	22.09	23.14
L_1	$C_{20}H_{18}N_6S_2$	406	288-290	268	White	84	59.09	58.88	4.46	4.30	20.67	21.34	15.78	16.45
L_2	$C_8H_{10}N_6S_2$	254	274-276	240	White	75	37.78	37.43	3.96	3.87	33.04	32.82	25.21	24.63
L_3	$C_{19}H_{14}N_6O_4$	390	180-183	338	Yellow	80	58.46	57.33	3.61	4.21	21.53	21.89	-	-

Table 2: Infrared spectra data of the prepared compounds and Ligands

Comp.	Structure	$\upsilon_{(N-H)}$	$\upsilon_{(S-H)}$	$\upsilon_{(C-H)ar.}$ $\upsilon_{(C-H)al.}$	$\upsilon_{(C=O)}$	$\upsilon_{(C=N)}$	$\upsilon_{(C=C)ar.}$ $\upsilon_{(C=C)al.}$	$\upsilon_{(C=S)}$
M_1	$C_6H_{12}N_4O_2$	3304 3202 3134	-	- 2879	1668	-	- 1647	-
M_2	$C_{20}H_{22}N_6O_2S_2$	3219	-	3027 2854	1675	-	1630 1569	1247
M_3	$C_8H_{14}N_6O_2S_2$	3370, 3262	-	- 2815	1645.5	-	- 1631	1164

		3187						
L_1	**$C_{20}H_{18}N_6S_2$**	-	2569	3074 2901	-	1566		1238
L_2	**$C_8H_{10}N_6S_2$**	3415 3188	2663	- 2919	-	1591	- 1614	1240
L_3	**$C_{19}H_{14}N_6O_4$**	3253	-	3014 2816	1730	1619	1504	-

Table 3: The ^{13}C-NMR spectrum of compound [L_1], can be categorized into three set of carbons into the following: the trizole ring carbon, the ethylenic group carbons, and the phenyl ring carbons.

Comp.	**Structure**	^{1}H-NMR (δ_H)	^{13}C-NMR
M_1	**$C_6H_{12}N_4O_2$**	2.25 (s, 6H, C=C-CH_3) for two methyl groups, 4.72 (s, br, 4H, NH_2), 8.78 (s, 2H, NH).	163.50 ppm (s, C=O), 123.50 ppm (s, -C=), 166.91 ppm (s, =C-) and 22.56 ppm (s, -CH_3) for ethylenic group.
M_2	**$C_{20}H_{22}N_6O_2S_2$**	2.23 (s, 6H, C=C-CH3) for two methyl groups, 7.42-7.92 (m, 10H, Ar-H), 8.15-8.23 (br, 2H, -NH-Ar), 9.20-9.92 (br, 2H, 4xNH).	163.35 ppm (s, C=O), 179.37 ppm (s, C=S), 123.45 ppm (s, -C=), 166.81 ppm (s, =C-)and 22.26 ppm (s, -CH_3) for ethylenic group. 131.71 ppm, 129.64 ppm, 126.94 ppm,and 130.13 ppm for Phenyl ring.
M_3	**$C_8H_{14}N_6O_2S_2$**	2.23 (s, 6H, C=C-CH3) for two methyl groups, 4.94 (s, br, 4H, NH_2), 7.98 (s, 2H, NH), 8.88 (s,2H, NH), 9.12 (s,2H, NH)	163.50 ppm (s, C=O), 180.57 ppm (s, C=S), 123.50 ppm (s, -C=), 166.91 ppm (s, =C-)and 22.56 ppm (s, -CH_3) for ethylenic group,
L_1	**$C_{20}H_{18}N_6S_2$**	2.28 ppm (s, 6H, C=C-CH_3) for two methyl groups; 3.08 ppm (s, 2H, S-H) for two thiol protons; 6.83-7.28 ppm (m, 10H, Ar-H) for two phenyl groups.	170.90 ppm (s, C1) and 146.69 ppm (s, C2) for triazole ring; 123.10 ppm (s, C3),167.91 ppm (s, C4), and 23.56 ppm (s, C5) for ethylenic group; 132.91 ppm (s, C6), 129.60 ppm (s, C7) , 127.82 ppm (s, C9), and 129.33 ppm (s, C8) for Phenyl ring
L_2	**$C_8H_{10}N_6S_2$**	2.18 ppm (s, 3H, C=C-CH3), δ_H 3.07 ppm (s, 1H, S-H), δ_H 4.25 ppm (s, 1H, N-H)	146.69 ppm (s, C2) and 162.39 ppm (s, C1) for triazole ring; 134.23 ppm (s, C3),13 for ethylenic group 1.51 ppm (s, C4), and 20.29 ppm (s, C5)
L_3	**$C_{19}H_{14}N_6O_4$**	2.28 ppm, (s, 2H, -CH_2-), δ_H =7.16 ppm, (s, 1H, C=N-N-H), δ_H =7.93 ppm, (s, 1H, -CO-N-H), 6.692-6.824 ppm, (m, 8H, Ar-H).	24.15 ppm (s, CH_2, C1), 172.24 ppm (s, C=O, C2), 135.31 ppm (s, N=C, C3), 118.71 ppm (s, C4), 127.40 ppm (s, C5), 123.40 ppm (s, C6), 130.21 ppm (s, C7), 130.21 ppm (s, C8), 130.21 ppm (s, C9) for phenyl isatin group, 168.44 ppm (s, C=O, C10) for isatin.

Metal complexes of the ligands L_1, L_2, and L_3 were prepared with the following metal ions: Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2}. These complexes are soluble in DMF and DMSO. The U.V., FT-IR absorption spectra of these complexes were recorded alongside with other physical properties such as melting points magnetic properties, and conductance of the complexes and were presented in tables 4 - 6. The molecularity of the prepared complexes were determined by following Mole ratio method to calculate (metal: ligand) ratio, and metal compositions of these complexes were determined by using flame atomic absorption spectrometry (Fig.3).^{13}C NMR spectrum of the ligand L_1 and^{1}H NMR spectrum of ligand L_2 are shown in figs. 4,5.The ratio (1:1) in the complexes Cr(III), Mn(II), Co(II), Ni(II), and Cu(II) with ligand (L_1), and Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with ligand (L_3). While complexes of ligand (L_2) with metals Cr(III) and Cu(II) ratio (1:1), the metals Mn(II), Co(II), and Ni(II) ratio (1:2) with same ligand.

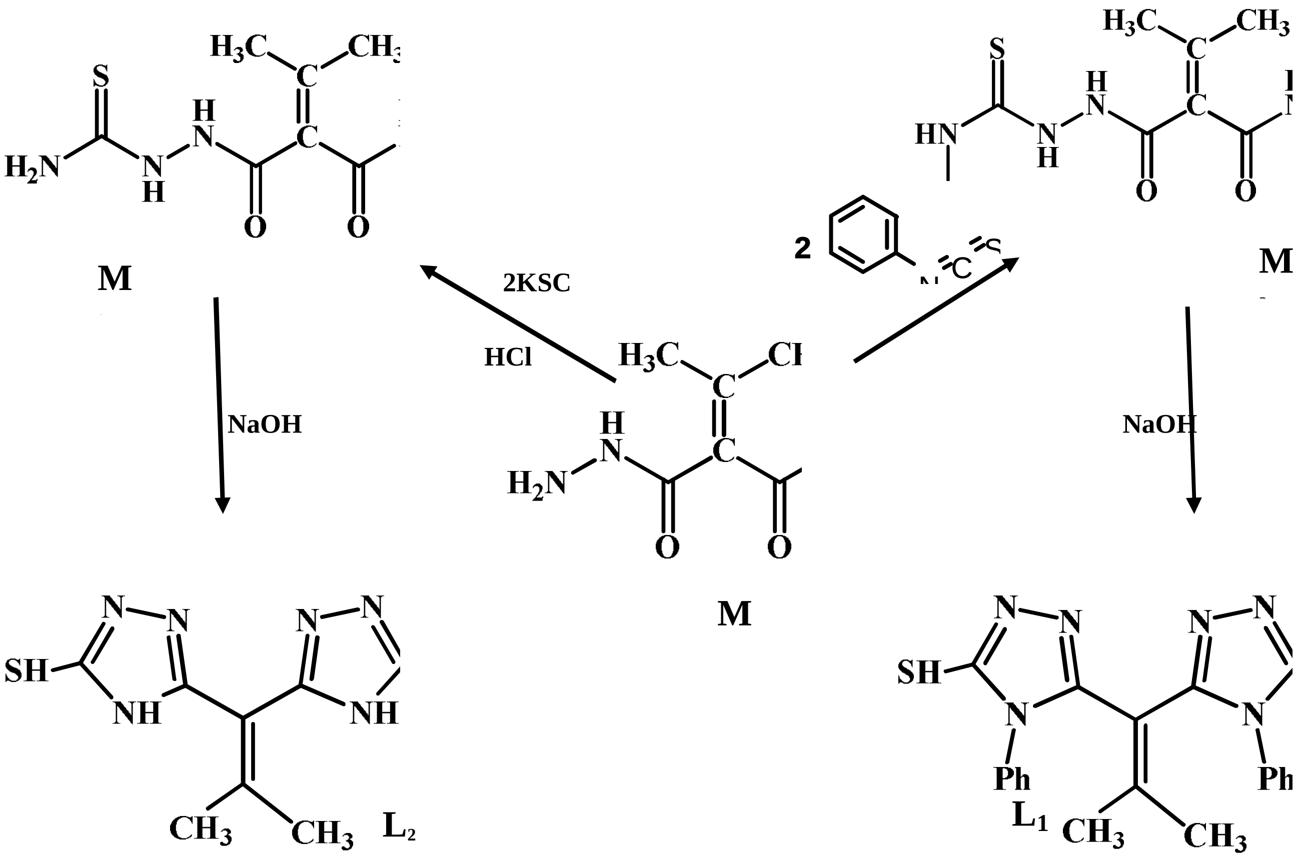


Figure 1: Preparation route of compounds M_2, M_2, M_3, L_1, and L_2.

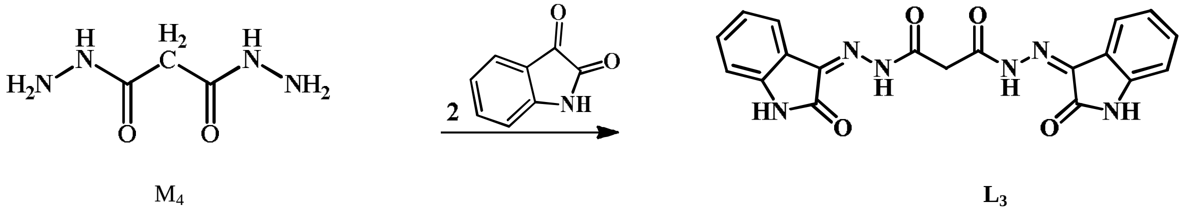


Figure 2: Preparation route for compound L_3.

Table 4: Physical properties for prepared complexes.

Complex Structure	M.p ^{0}C	▯ (nm)	Color	% Yield	Metal % Found (Calc.)
		$C_{20}H_{16}N_6S_2$ (L_1)			
[Cr($C_{20}H_{16}N_6S_2$)(H_2O)$_2$]Cl	287-290*	348	Green light	51	9.85 (10.56)
[Mn($C_{20}H_{16}N_6S_2$)(H_2O)$_2$]	258- 261*	327	Yellow mustard	63	10.8 (11.09)
[Co$_2$($C_{20}H_{16}N_6S_2$)2(H_2O)$_4$]	273-276 *	420	Blue	77	11.64 (11.80)
[Ni($C_{20}H_{16}N_6S_2$) (H_2O)$_2$]	215-218 *	305	Yellowish green	69	10.92 (11.76)
[Cu$_2$($C_3H_6N_6S_2$)(H_2O)$_4$]	285-288 *	262	Light brown	83	16.13 (16.42)

$C_8H_{10}N_6S_2$ (L_2)					
[$Cr(C_8H_{10}N_6S_2)(H_2O)_2Cl_2$]Cl	274-276*	385	Green	55	14.97 (15.28)
[$Mn(C_8H_{10}N_6S_2)(H_2O)_2$]	280-282*	343	Yellowish green	69	15.35 (16.00)
[$Co_2(C_8H_{10}N_6S_2)_2(H_2O)_4$]	228-230*	327	Gray	62	14.92 (16.97)
[$Ni(C_8H_{10}N_6S_2)_2(H_2O)_2$]	210-212 *	325	Yellowish green	74	16.53 (16.91)
[$Cu_2(C_8H_{10}N_6S_2)_2(H_2O)_4$]	214-216*	324	Dark olive green	85	16.44 (18.06)
$C_{19}H_{14}N_6O_4$ (L_3)					
[$Co(C_{19}H_{14}N_6O_4)$] Cl_2	270-272*	360	Reddish brown	76	6.39 (7.02)
[$Ni(C_{19}H_{14}N_6O_4)$] Cl_2	255-252*	.368	Orange	40	11.42 (12.11)
[$Cu(C_{19}H_{14}N_6O_4)$] Cl_2	260-262*	350	Dark orange	76	13.41 (12.99)

*decomposition

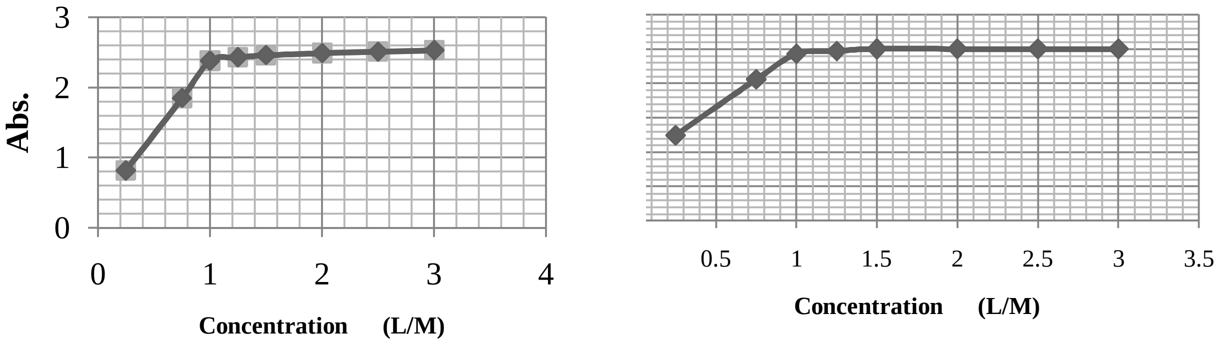
Table 5: The characteristic electronic spectra of the ligand (L_1) and its metal complexes

Compounds	**λ_{max} (nm)**	**λ cm^{-1}**	**Assignment**
$C_{20}H_{16}N_6S_2$ (L_1)	268 211	37313 47393	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
[$Cr(C_{20}H_{16}N_6S_2)(H_2O)_2$]Cl	640 348 281	15625 28735 35587	${}^4A_2g(F) \rightarrow {}^4T_2g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(P)$
[$Mn(C_{20}H_{16}N_6S_2)(H_2O)_2$]	442 327	22624 30581	${}^6A_1g \rightarrow {}^4T_2g$ ${}^6A_1g \rightarrow {}^4Eg$, ${}^4A_1g(G)$
[$Co(C_{20}H_{16}N_6S_2)(H_2O)_2$]	690 540 420	14492 18518 23809	${}^4T_1g \rightarrow {}^4T_2g$ (F) ${}^4T_1g \rightarrow {}^4T_1g$ (P) ${}^4A_1g$ (F) $\rightarrow {}^4T_2g$
[$Ni(C_{20}H_{16}N_6S_2)$ $(H_2O)_2$]	631 407 305	15847 24549 32786	$A_2g(F) \rightarrow {}^4T_2g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(P)$
[$Cu_2(C_{20}H_{16}N_6S_2)_2(H_2O)_4Cl_2$]	621	16339	${}^2Eg \rightarrow {}^2T_2g$
$C_8H_{10}N_6S_2$ (L_2)	247 210	40485 47619	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$
[$Cr(C_8H_{10}N_6S_2)(H_2O)_2Cl_2$]Cl	640 385 291	15625 25974 34364	${}^4A_2g(F) \rightarrow {}^4T_2g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(F)$ ${}^4A_2g(F) \rightarrow {}^4T_1g(P)$
[$Mn(C_8H_{10}N_6S_2)_2(H_2O)_2$]$Cl_2$	699 424	14306 23584	${}^6A_{1g} \rightarrow {}^4T_2g$ ${}^6A_{1g} \rightarrow {}^4Eg$ ${}^4A_{1g}$ (G)
[$Co(C_8H_{10}N_6S_2)_2(H_2O)_2$]$Cl_2$	652 383 367	15337 26109 27174	${}^4T_1g(F) \rightarrow {}^4T_2g(F)$ ${}^4T_1g(F) \rightarrow {}^4T_1g(P)$ ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$
[$Ni(C_8H_{10}N_6S_2)_2$]Cl_2	770 362 368	12870 24570 27173	${}^1A_1g \rightarrow {}^1A_2g$ ${}^1A_1g \rightarrow {}^1B_1g$ ${}^1A_1g \rightarrow {}^1Eg$
[$Cu_2(C_8H_{10}N_6S_2)_2(H_2O)_4Cl_2$] Cl_2	880	11358	${}^2Eg \rightarrow {}^2T_2g$
$C_{19}H_{14}N_6O_4$ (L_3)	352 247	28409 40485	$n \rightarrow \pi^*$ $\pi \rightarrow \pi$
[$Co(C_{19}H_{14}N_6O_4)$]Cl_2	653 409 267	15313 24449 37543	${}^4T_1g(F) \rightarrow {}^4T_2g(F)$ ${}^4T_1g(F) \rightarrow {}^4T_1g(P)$ ${}^4T_1g(F) \rightarrow {}^4A_2g(F)$

$[Ni(C_{19}H_{14}N_6O_4)]Cl_2$	779 572 368	12836 17482 27155	${}^3A_2g(F) \rightarrow {}^3T_2g(F)$ ${}^3A_2g(F) \rightarrow {}^3T_1g(F)$ ${}^3A_2g(F) \rightarrow {}^3T_1g(P)$
$[Cu(C_{19}H_{14}N_6O_4)]Cl_2$	467 324 283	21413 30864 35335	${}^2B_1g \rightarrow {}^2A_1g$ ${}^2B_1g \rightarrow {}^2B_2g$ ${}^2B_1g \rightarrow {}^2Eg$

Table 6: Magnetic susceptibility for Complexes of ligands L_1, L_2, and L_3, and the molar conductivity for in the (DMSO)

$C_{20}H_{16}N_6S_2$ (L_1) Complexes	**μ_{eff} (B.M)**	**Λ_m (Ω^{-1} cm^2 mol^{-1})**	**Ratio**	**Possible Geometry**
$[Cr(C_{20}H_{16}N_6S_2)(H_2O)_2]Cl$	3.62	38	1:1	O.h
$[Mn(C_{20}H_{16}N_6S_2)(H_2O)_2]$	5.97	14	Non Elec.	O.h
$[Co_2(C_{20}H_{16}N_6S_2)_2(H_2O)_4]$	4.31	8	Non Elec.	O.h
$[Ni(C_{20}H_{16}N_6S_2)(H_2O)_2]$	3.03	7	Non Elec.	O.h
$[Cu_2(C_{20}H1_6N_6S_2)_2(H_2O)_4]$	1.80	12	Non Elec.	O.h
$C_8H_{10}N_6S_2$ (L_2) Complexes	**μ_{eff} (B.M)**	**Λ_m (Ω^{-1} cm^2 mol^{-1})**	**Ratio**	**Possible Geometry**
$[Cr(C_8H_{10}N_6S_2)(H_2O)_2]Cl$	3.31	38	1:1	O.h
$[Mn(C_8H_{10}N_6S_2)_2(H_2O)_2]$	5.84	9	Non Elec.	O.h
$[Co_2(C_8H_{10}N_6S_2)_2(H_2O)_4]$	4.40	7	Non Elec.	O.h
$[Ni(C_8H_{10}N_6S_2)_2(H_2O)_2]$	3.41	14	Non Elec.	O.h
$[Cu_2(C_8H_{10}N_6S_2)_2(H_2O)_4]$	1.75	18	Non Elec.	O.h
$C_{19}H_{14}N_6O_4$ (L_3) Complexes	**μ_{eff} (B.M)**	**Λ_m (Ω^{-1} cm^2 mol^{-1})**	**Ratio**	**Possible Geometry**
$[Co(C_{19}H_{14}N_6O_4)]Cl_2$	4.82	77	1:2	O.h
$[Ni(C_{19}H_{14}N_6O_4)]Cl_2$	3.20	70	1:2	O.h
$[Cu(C_{19}H_{14}N_6O_4)]Cl_2$	1.87	70	1:2	O.h



(a) Molar ratio for CrL_1 at λ_{max} = 348 nm **(b) Molar ratio for MnL_1 at λ_{max}= 327 nm**

Figure 3: Application of the Molar ratio method to obtain the molecularity of the prepared complexes

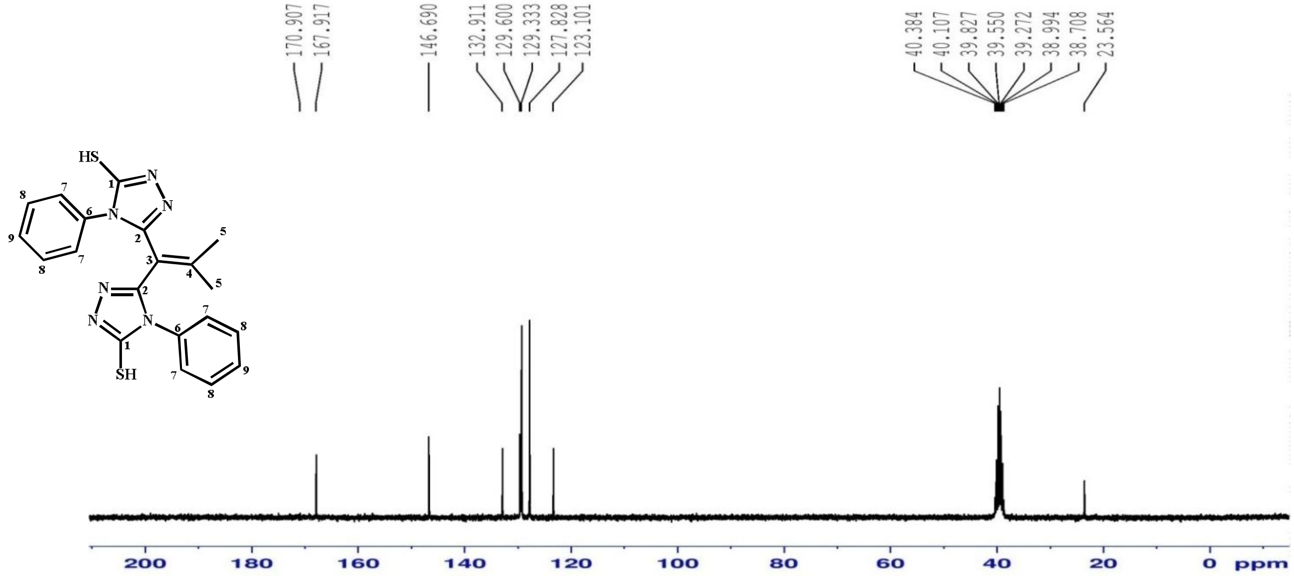


Figure 4: ^{13}C NMR spectrum of the ligand L_1

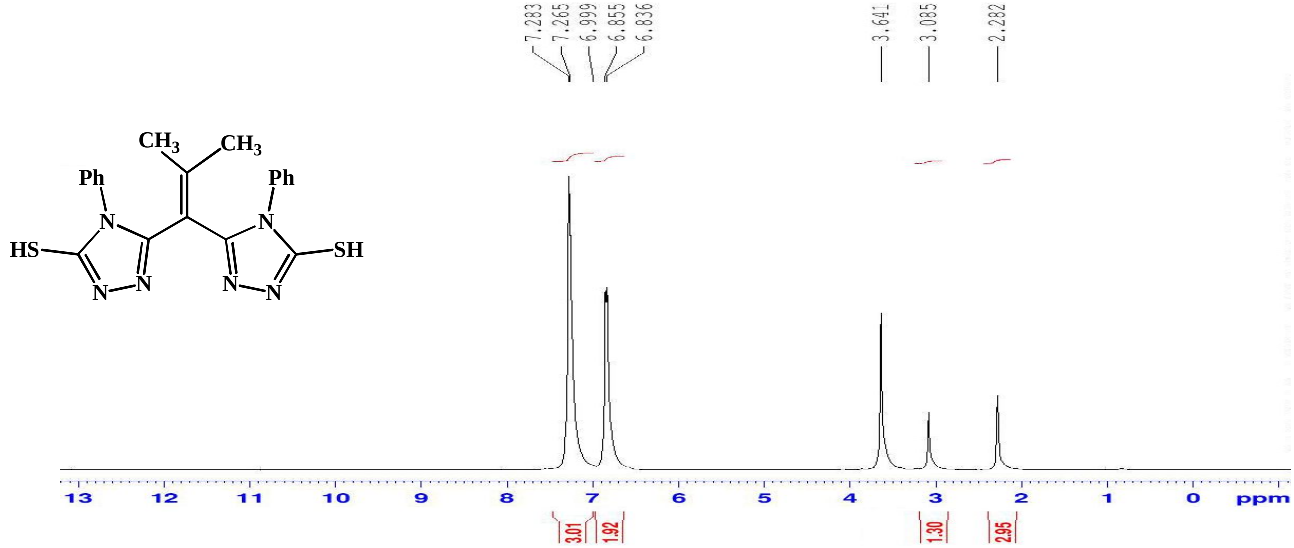


Figure 5: ^{1}H NMR spectrum of ligand L_2

The FT-IR absorption spectra of the ligand L_1 and their transition metal complexes (Cr^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) were presented in table 5. In these spectra the azomethine C=N band was shifted from 1566 cm^{-1} to a band within the range from 1613 to 1624 cm^{-1}. Thiol S-H band at 2569 cm^{-1} (weak) was disappeared for all the prepared complexes. All these complexes exhibit new absorption bands stand for the bonds $\mathbf{\nu_{C=S}}$ and $\mathbf{\nu_{N\text{-}C=S}}$ bands, due to the reduction of the sp^2 hybridization of sulfur neighboring C=N double. These absorptions were further supported by the appearance of new $\mathbf{\nu_{M\text{-}S}}$, and $\mathbf{\nu_{M\text{-}N}}$. The assignment of the ν_{C-N} bands was not easy, due to the presence of four C-N bands at different positions also the assignment of the N-N was not well resolved and was found to be overlapped with another peaks in the same range. FT-IR spectra for the ligand L_3 showed a sharp absorption band around 3200 cm^{-1} attributed to the presence of N-H bond a very strong band near 1700 cm^{-1} assigned to C=O stretching vibration. All the IR spectra of exhibited shifted band at 1622 - 1602 cm^{-1} for the azomethine C=N, compared with the free ligand viz. 1596 - 1503 cm^{-1}. The broad band that appears in the range of 3160–3210 cm^{-1} is assigned to the stretching vibration of ring N−H. The strong absorption bands at 1702 cm^{-1} and 1627 cm^{-1} in the free ligand due to $\upsilon_{C=O}$, in the complexes spectra, this band have been found in the range between 1696 - 1655 cm^{-1}, which indicates the coordination of the oxygen atom at the $\upsilon_{C=O}$ group. A broad band was observed at 3200-3500 cm^{-1} in all the spectra of complexes, assigned to a ν_{O-H} and related to the presence of water molecules in the crystal lattice of the complexes [30-33].

Electronic spectral data of the ligand and their transition metal complexes were recorded in DMSO solutions. Most of the transition metal complexes are colored as an indication to the occurrence of coordination. The complexes show different characteristic λ_{max}, compared with the ligand and this was another indication for occurrence of coordination [34-38]. The electronic spectra of the complexes exhibit absorption bands at λ_{max} within the region 11358 - 37543 cm^{-1} corresponding different type of transitions respectively, and the value of the λ_{max} and their assignments are listed in table 5. The magnetic moments μ_{eff} obtained for these complexes at room temperature are within the range 1.80 - 5.97 BM, and are listed in table 6. The magnetic moment μ_{eff} value of the complexes $[Cr(C_{20}H_{16}N_6S_2)(H_2O)_2]Cl$ and $[Cr(C_8H_{10}N_6S_2)(H_2O)_2]Cl$, were 4.55, and 4.29 BM, and these values were in agreement with that expected for octahedral for chromium metal[39-41]. The μ_{eff} values for the complexes $[Mn(C_{20}H_{16}N_6S_2)(H_2O)_2]$, $[Mn_2(C_8H_{10}N_6S_2)(H_2O)_2Cl_2]$, and $[Mn(C_{19}H_{14}N_6O_4)_2]Cl_2$ were 3.22, 3.03, and 3.10 BM respectively, while $[CuL_1Cl_2]$, $[CuL_2Cl_2(H_2O)]$, $[CuL_3Cl_2(H_2O)]$ and $[CuL_4Cl_2(H_2O)]$ have the values 1.74, 1.72, 1.77 and 1.75 BM respectively, and these values were in agreement with high spin configuration. The conductivity measurements have been used in coordination chemistry to identify the ionic compound formula in solution or solid state. The molar conductance of the complexes with ligand L_1, L_2, and L_3 were measured in DMSO and found to be in the range 15 - 24.5 $S.cm^2mole^{-1}$, 13.02 - 21 $S.cm^2mole^{-1}$, 13.9 - 21.01 $S.cm^2.mole^{-1}$ and 10 - 23 $S.cm^2mole^{-1}$, respectively. This result indicated the non-electrolyte nature of these complexes, as shown in table 6. The molar conductance values are too low to account for any dissociation of the complexes in DMSO. Hence, these complexes can be regarded as non-electrolytes in DMSO.

From these measurements may suggest the following configuration for these complexes: (a) octahedral geometry for the formula: $[M(L_1)(H_2O)Cl]Cl$ ($M = Cr^{+3}$), and $[M(L_1)(H_2O)]$ ($M = Mn^{+2}, Ni^{+2}$), (b) octahedral geometry with dimmer structure for the formula: $[M_2(L^*)_2(H_2O)_4Cl_2]\,Cl_2$ (where $L^* = L_1, L_2$. $M = Co^{+2}, Cu^{+2}$), and (c) octahedral geometry of the formula $[M(L_3)]Cl_2$ ($M = Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2}$ and Cu^{+2}) and proposed structures shown in fig.6.and fig7.

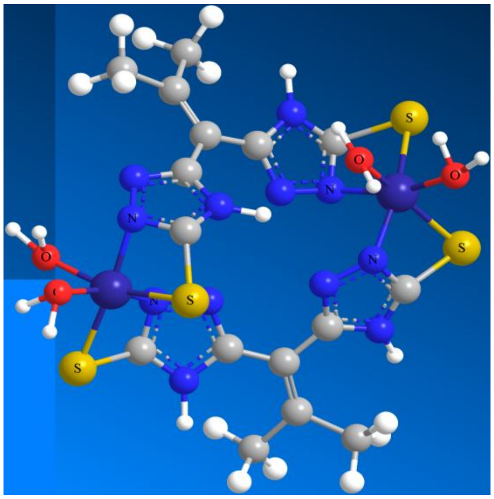


Figure 6: The proposed molecular structure of Cu^{2+} and Co^{2+} complexes dimer with L_1 or L_2.

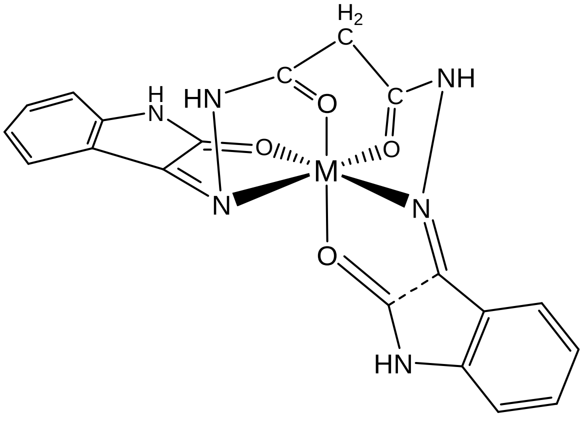


Figure 7: The proposed molecular structure of M^{2+} complexes with L_3.

APPLICATIONS

The bactericidal activity of these complexes were determined for four local strains of pathogenic bacteria: *Escherichia Coli*, *Staphylococcus aureus*, *Proteus mirabilis*, and *Pseudomonas aeruginosa*, The antibiotics used (AX, CN and TE) as reference in this study, some of these compounds exhibit the effectiveness of anti-Microbial (tab.7).

	Escherichia Coli								***Staphylococcus aureus***								***Proteus***								***Pseudomonas aeruginosa***							
	1	**2**	**3**	**4**	**5**	**AX**	**CN**	**TE**	**1**	**2**	**3**	**4**	**5**	**AX**	**CN**	**TE**	**1**	**2**	**3**	**4**	**5**	**AX**	**CN**	**TE**	**1**	**2**	**3**	**4**	**5**	**AX**	**CN**	**TE**
CrL_1	-	-	-	-	-	++	++	+	+	+	+	-	-	-	++	++	+	-	-	-	-	+	++	+	-	-	-	-	-	-	++	-
MnL_1	-	-	-	-	-	++	++	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	++	+	+	+	+	+	+	-	++	-
CoL_1	-	-	-	-	-	++	+++	+	-	-	-	-	-	+	+++	++	-	-	-	-	-	-	+	-	-	-	-	-	-	+	+	+
NiL_1	-	-	-	-	-	++	++	+	+	+	-	-	-	++++	++++	++++	+	-	-	-	-	+	++	+	+	-	-	-	-	-	++	-
CuL_1	-	-	-	-	-	++	++	+	+	+	-	-	-	++++	++++	++++	+	-	-	-	-	+	++	+	+	+	+	+	+	-	++	-
CrL_2	-	-	-	-	-	++	++	+	+	-	-	-	-	-	++	+++	-	-	-	-	-	+	++	+	-	-	-	-	-	-	+	-
MnL_1	-	-	-	-	-	++	++	+	-	-	-	-	-	+	+	+	-	-	-	-	-	+	++	-	-	-	-	-	-	-	+	-
Co	-	-	-	-	-	++	+	+	+	+	+	-	-	+	+	+	-	-	-	-	-	+	+	+	-	-	-	-	-	-	+	+

L_1							+							+	++								+								+	
Ni L_1	+	+	+	+	+	++	++	+	+	-	-	-	-	+	++	+	-	-	-	-	-	-	+	-	-	-	-	-	-	+	+	+
Cu L_1	-	-	-	-	-	+++	+++	+	+	+	-	-	-	+++	+++	+++	+	+	-	-	-	+	++	+	+	-	-	-	-	-	++	-
Co L_3	-	-	-	-	-	+++	++	+	-	-	-	-	-	-	++	+++	+	-	-	-	-	+	++	+	-	-	-	-	-	-	++	+
NiL_3	-	-	-	-	-	+++	++	+	+	+	+	+	+	++	++	+	+	-	-	-	-	-	++	-	+	-	-	-	-	-	++	+
CuL_3	-	-	-	-	-	++	+++	+	+	+	+	+	+	+	++	+	-	-	-	-	-	+	++	+	-	-	-	-	-	-	++	-

CONCLUSIONS

Three ligands were synthesized from the reactions of *iso*propylidene diethyl malonate or *di*ethyl malonate hydrazides to form two heterocyclic rings of *1,2,4*-triazoles [L_1, *5,5'*-(2-methylprop-1-ene-*1,1*-diyl)*bis*(4-phenyl-*2,4*-dihydro-3H-*1,2,4*-triazole-*3*-thione)], [$L_{2,}$ *5,5'*-(2-methylprop-1-ene-1,1-diyl)*bis*(*2,4*-dihydro-3H-*1,2,4*-triazole-*3*-thione)], and isatine Schiff base [$L_{3,}$ *N'1,N'3-bis*[(3E)-2-oxo-*1,2*-dihydro-3H-indol-*3*-ylidene]propanedihydrazide]. These ligands coordinate to following metal ions; Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2}, with the following configuration for these complexes: (a) octahedral geometry for the formula: $[M(L_1)(H_2O)Cl]Cl$ (M = Cr^{+3}), and $[M(L_1)(H_2O)]$ (M = Mn^{+2}, Ni^{+2}), (b) octahedral geometry with dimmer structure for the formula: $[M_2(L^*)_2(H_2O)_4Cl_2]\ Cl_2$ (where L* = L_1, L_2. M = Co^{+2}, Cu^{+2}), and (c) octahedral geometry of the formula $[M(L_3)]Cl_2$ (M = Cr^{+3}, Mn^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2}).

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