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SYNTHESIS, CHARACTERIZATION AND THEORETICAL STUDIES OF [(4-AMINO-5-(2-(6-METHOXYNAPHTHALEN-2-YL)PIPERIDINO)-1,2,4-TRIAZOLE-3-THION] WITH Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) METAL IONS

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ABSTRACT

A new ligand (4-amino-5-(2-(6-methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion (L), was synthesized by treating 2-(6-methoxynahthalen-2-yl) propanoic acid) hydrazides successively with alcoholic potassium hydroxide-carbon disulfide and hydrazine hydrate. It was characterized by using FT-IR spectroscopy, UV-visible spectroscopy, C. H. N. S, G. Mass, and ^{1}H-NMR spectroscopy. The prepared complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal ions were characterized quantitatively and qualitatively by using: micro elemental analysis, FT-IR spectroscopy, UV-visible spectroscopy, C. H. N. S., magnetic susceptibility and conductivity measurements. Structural geometries of complexes were suggested in solid state and in gas phase by using theoretical treatments, using (Hyper Chem. 8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔH^o_f) and binding energy (ΔE_b) for free ligand (L) and their metal complexes were calculated by PM3 method at 298 K. Furthermore, the electrostatic potential of the free ligand (L) was calculated to investigate the reactive sites of the molecules. PM3 was used to evaluate the vibration spectra of the free ligand (L) and its metal complexes, and the theoretically calculated wave numbers were compared with the experimented values. The theoretically obtained frequencies agreed well with those found experimentally, and in addition, calculations helped to assign unambiguously the most diagnostic bands. Bond length were calculated by using PM3 method.

Key words: Triazole, Metal complexes, Theoretical treatment.

INTRODUCTION

Heterocyclic compounds are considered one of an important type of organic compounds due to their implication in drugs and industrial studies[1-3]. Triazoles are five memberd heterocyclic compounds with molecular formula C_2H_3N containing three nitrogen and two carbon atoms[4,5]. Triazole are considered to be good coordinating ligands[6], because they involved both; hard nitrogen and soft sulfur atom as thioamide group. These ligands have donor group that coordinate with wide range of metal ions[7]. In this paper, a new

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thione-triazole was prepared and used as a ligand to prepare new metal complexes by reaction with metals Co (II), Ni(II), Zn(II), Cu(II) and Cd(II). Complexes with (4-amino-5-(2-(6 methoxynaphthalen-2-yl)piperidino)-1,2,4-triazole-3-thion are described with theoretical study in the gas phase by using semi-empirical method in order to show the most stable conformation and to the results were compared with the experimental data. The study aims to calculate the heat of formation and binding energy for all the probable geometries and to find the most active sites of the ligand (**L**) by using the electrostatic potential calculations.

EXPERIMENTAL

Materials

All chemicals were of highest purity and used as received. Melting points were recorded on a Gallenkamp MF B600 010F melting point apparatus. Elemental analyses (C.H.N.S) were obtained using EA-034.mth. for ligand and their metal complexes. Metal contents of complexes were estimated spectrophotometrically using Flame atomic absorption Shimadzu-670 AA Spectrophotometer. Infrared spectra were recorded using FT-IR-8300 Shimadzu in the range of 4000-400 cm^{-1}. Magnetic susceptibilities of samples in the solid state were measured by using a Bruker BM6 magnetic balance. The molar conductivity was measured by using Electrolytic Conductivity Measuring set Model MC-1-Mark V by using platinum electrode (EDC 304) with cell constant (1 cm^{-1}), concentration (10^{-3} M) in dimethylformmide as a solvent at room temperature. Electronic spectra were obtained using UV-1650PC-Shimadzu spectrophotometer at room temperature. The measurement were made using a concentration (10^{-3} M) of the (L) ligand and their metal complexes in dimethylformmide as a solvent.

Synthesis of ligand[8-10]

Preparation of (2-(6-methoxynaphthalen-2-yl) propanoate) (A_1)

Sulphuric acid (8 mL) was added dropwise with continuous stirring to a solution of carboxylic acid (2-(6-methoxynahthalen-2-yl) propanoic acid) (0.1 mol) in 200 mL ethanol. The mixture was heated under reflux for 10 hrs. On cooling, the mixture was poured on to crushed ice, the precipitated crystalline solid was filtered, washed with water, followed by 10% sodium hydrogen carbonate solution and finally with water. Then the crude product was recrystallized from ethanol to give 84% yield of compound (A_1), off white crystal with melting point (103-105)^{o}C.

Preparation of (2-(6-methoxynaphthalen-2-yl)propanohydrazide (A_2)

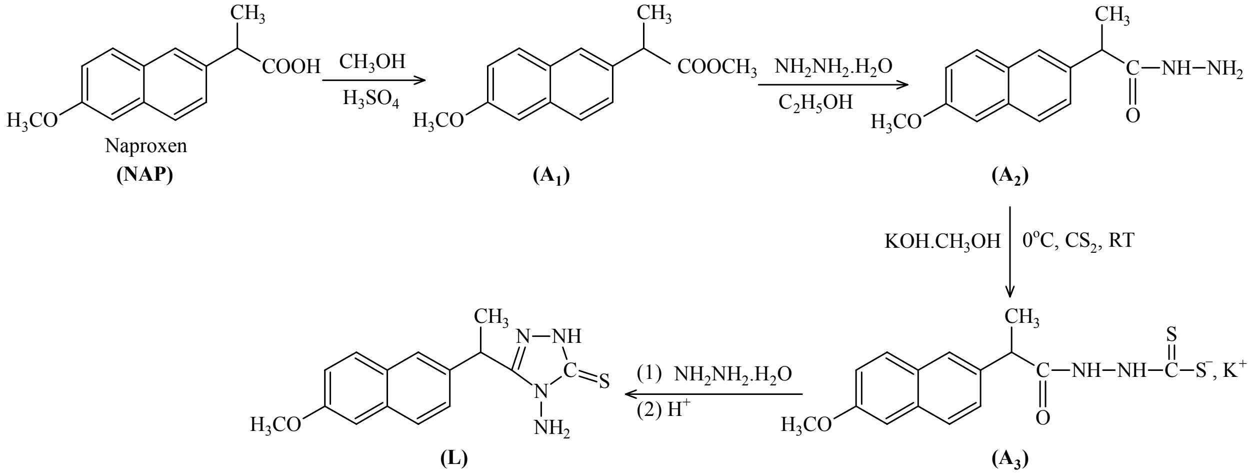
Ester (A_1) (0.1 mol) was dissolved in absolute ethanol (50 mL). To the above solution, hydrazine hydrate 80% (0.1 mol was added). The resulting reaction mixture was refluxed on a steam bath for 10-12 hrs. On cooling, cold water (150 mL) was added to the mixture and the separated white crystalline solid was filtered, washed with cold water, dried and crystallized from ethanol, to give 82% yield of white colored compound (A_2), with melting point (135-137)^{o}C.

Preparation of ((2-(6-methoxynaphthalen-2-yl) propanoyl) hydrazine carbodithioate (A_3)

Compounds (A_2) (0.05 mol) was treated with a solution of potassium hydroxide (0.0643 mol) in ethanol (70 mL) at 0^{o}C with stirring. Then (7 mL) of carbon disulfide was added dropwise and the reaction mixture was stirred overnight at room temperature. The solid product (A_3) was filtered, washed with cold methanol and dried.

Preparation of ligand (4-amino-5-(2-(6-methoxynaphthalen-2yl)piperidino)-1,2,4-triazole-3-thione (L)

A mixture of compound (A_3) (0.05 mol) and 80% hydrazine hydrate (10 mL) was heated under reflux till the evolution of hydrogen sulphide completely ceases (about 6 hrs). On cooling, water (200 mL) was added and the mixture was neutralized with 10% hydrochloric acid and allowed to stand for three hrs. The separated crude product was filtered, washed with water, dried and crystallized from ethanol, to give 80% yield of compound (L), which was a white powder with melting point (210-212)^{o}C.



Scheme 1: Synthesis of Ligand (L)

Preparation of metal complexes of (L) (G_1 – G_5)

The salts of [$Co(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$, $Cu(CH_3COO)_2.H_2O$, $Zn(CH_3COO)_2.2H_2O$ and $Cd(CH_3COO)_2.2H_2O$] were dissolved separately in ethanol and added to an ethanolic solution of L in (1:2) (metal : ligand) mole ratio with stirring. The mixture was heated under reflux for 4 hrs. During this period, the precipitation was completed. The product was then collected by filtration, washed with ethanol and dried under vacuum for 2 hrs.

C-Programs used in theoretical calculations

Hyperchem-8 is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use[11,12]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation. This information is useful in determining reactivity and correlating calculated results with experimental data.

Computational methods

(a) Semi-empirical quantum mechanical

(b) Molecular mechanics

(c) Mopac 2000

Types of calculations

The types[13,14] of prediction possible of molecules are:

(a) Geometry optimization calculations employ energy minimization algorithms to locate stable structures.

(b) Bond distances

(c) Molecular dynamics, which provide the thermodynamic calculations and dynamic behavior of molecules

(d) Plot the electrostatic potential field (HOMO and LUMO).

(e) Vibrational spectrum (I.R and Raman spectra).

RESULTS AND DISCUSSION

Elemental analysis

The interaction of ligand (L) with the metal ions study in ethanol gave a crystalline product with different colors depending on the metal ions, All complexes were readily soluble in $CHCl_3$, DMF and DMSO and were found to be stable towards air and moisture, but they were decomposed before melting. The physical analytical data of (L) and it's metal complexes (G_1-G_5) are given in Table 1. Results obtained from elemental analysis (C. H. N. S) and flame atomic absorption are in a satisfactory agreement with the calculated values. The suggested molecular formula also supported by spectral (FT-IR) and (Uv-Vis) analysis, magnetic susceptibility and conductivity measurements.

Table 1: Physical data of ligand (L) and its metal complexes (G_1-G_5)

Comp. No.	Color	Melting point	Yield %	Elemental analysis found/Calc.					Suggested formula
				C%	H%	N%	S%	M%	
L	white	210-212	75	60.00 60.24	5.33 6.12	18.67 19.15	10.67 11.54	-	($C_{15}H_{16}N_4SO$)
[G_1]	Dark brown	240d	88	52.52 53.14	4.89 5.23	14.42 15.18	8.24 9.0	7.58 7.43	[$Co(C_{30}H_{32}N_8S_2O_2)(CH_3COO)_2$]
[G_2]	Light green	255d	80	52.53 52.97	4.89 5.16	14.42 15.02	8.24 8.85	7.56 7.21	[$Ni(C_{30}H_{32}N_8S_2O_2)(CH_3COO)_2$]
[G_3]	Dark green	280d	86	52.21 53.11	4.86 4.99	14.33 14.86	8.19 9.11	8.13 8.32	[$Cu(C_{30}H_{32}N_8S_2O_2)$]$(CH_3COO)_2$
[G_4]	Off white	198d	92	52.08 52.69	4.85 5.14	14.29 14.63	8.17 9.11	8.35 8.42	[$Zn(C_{30}H_{32}N_8S_2O_2)$]$(CH_3COO)_2$
[G_5]	Off white	210d	88	49.16 50.02	4.58 4.94	13.49 13.81	7.71 8.12	13.54 13.04	[$Cd(C_{30}H_{32}N_8S_2O_2)$]$(CH_3COO)_2$

Proton nuclear magnetic resonance spectrum of L

The nuclear magnetic resonance spectrum of the newly synthesized ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of ^1H NMR chemical shifts. The spectrum was determined in d_6, DMSO solution as an internal reference. According to the results obtained from the chemical shifts in spectrum, the molecular structure of the ligand can be illustrated[19,20], $\delta H_{(1)}$ = 1.567 ppm (3H, d, CH_3), $\delta H_{(2)}$ = 3.86 ppm (1H, q, CH), $\delta H_{(3)}$ = 3.87 ppm (3H, s, OCH_3), δ $H_{(4)}$ = 5.3 ppm (2H, s, NH_2), δ Ph = 7.07-7.67 ppm (6H) Fig. 1.

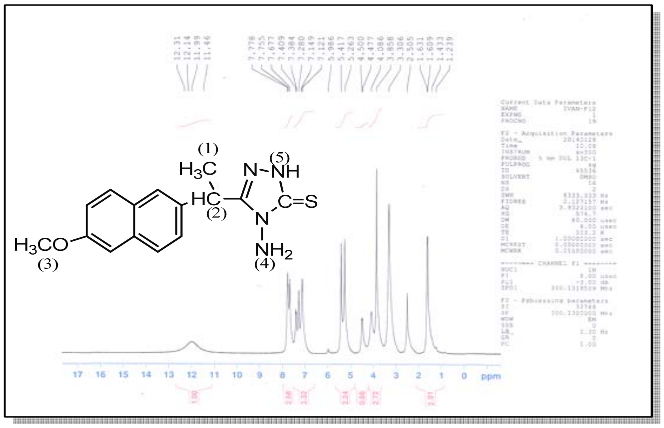


Fig. 1: The ^{1}H-NMR spectral of L

Infrared spectroscopic study[15-18]

The spectra of L and its complexes with their respective assignments are shown in Table 2. L exhibited the diagnosis ν(C=S) at 1041, (νas NH_2 and νs NH_2) at 3265 and 3211, (δ NH) at 3441, (δ NH) at 1595, cm^{-1}. In all complexes [G_1---G_5], the ligand (L), the characteristic stretching vibration modes concerning (L) and its metal complexes are described in Table 4. L exhibited bands, at 3439, 3209, 3269, 1643 and 1041, cm^{-1}. These can be assigned to ν(NH), (νsNH_2 and νas NH_2), and νC=N, νC=S, respectively. Ligand behaves as bidentate coordinating with metal through sulfur of thiocarbonyl and nitrogen of amino group, and therefore, the bands due to ν(C=S), (νs and νas of NH_2) bands were shifted to lower frequency (Table 2), as well as a new bands for complexes (G_1-G_2) in the region 1521, 1537 cm^{-1}, which may be assigned to the asymmetric vibration of coordinated carboxylate groups (νas COO^-) and the bands in the region 1302-1305 cm^{-1} may be attributed to the symmetric vibration of carboxylate group (**ν**s COO^-). The large differences between the frequencies of [**ν**as(COO^-)] and [**ν**s(COO^-)], [$\Delta\nu > 200$ cm^{-1}] in (G_1 and G_2) complexes are indicative of the involvement of the coordination of the carboxylate groups to the metal ion in a monodentate fashion. On Comparison with (G_1) and (G_2) complexes, the newly synthesized copper, zinc and cadmium complexes [G_3, G_4 and G_5] show appearance of new bands in the region 1655-1665 cm^{-1}, which may be assigned to the vibration of uncoordinated carboxylate group. Other low intensity bands observed in the region 445-460, 518-520 and 523-544 cm^{-1} are attributed to ν(M-S) and ν(M-N), respectively in the all complexes except (G_1 and G_2) and ν(M-O) in the case of ($G_1$and G_2) complexes modes, respectively.

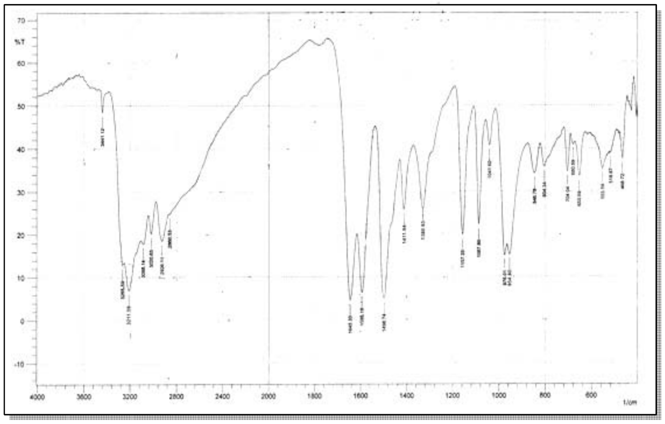


Fig. 2: IR spectra of ligand

Table 2: The most diagnostic FT-IR bands of L and its metal complexes (G_1-G_5)

Comp. No.	$\upsilon_{C=S}$	$\upsilon_{C=N}$	ν_{NH_2} (as, s)	ν_{NH}	$\upsilon_{M\text{-}N}$	$\upsilon_{M\text{-}O}$	$\upsilon_{M\text{-}S}$	υ_{COO^-} asysym	ν_{COO^-} uncoord
L	1041	1645	32653211	3441	-	-	-	-	-
(G_1)	1022	1642	32503233	3439	532	535	450	1510 1302	-
(G_2)	1030	1645	32593192	3442	529	544	445	1511 1304	-
(G_3)	1020	1644	32523100	3441	528	-	458	-	1668
(G_4)	1029	1641	32523198	3441	531	-	454	-	1666
(G_5)	1030	1641	32593200	3442	530	-	452	-	1668

Electronic spectra[19-21], magnetic moment and conductance

The electronic spectra of the metal complexes were recorded in chloroform in the range of 200-1100 nm.

G_1: The measured magnetic moment was (4.0 B.M), which this shows that the cobalt ion in, its bluish brown complex is typical of d^7 system with three unpaired electrons indicating a quartet state and suggest high spin octahedral geometry. The electronic spectrum of the brown (G_1) complex in chloroform exhibited two bands at 15174 and 19157 cm^{-1}, assignable to $^4T_1g \rightarrow {}^4A_2g_{(F)}$ and $^4T_1g \rightarrow {}^4T_1g_{(P)}$ transitions, respectively for an octahedral geometry of Co(II). The value of various ligand filed parameters (B^-, ν_1, Dq, β and 10 Dq) have been calculated using Tanabe-Sugano diagram for d^7 system and found to be 583.6, 6886.5, 933.76, 0.601 and 9337.6, respectively. The molar conductivity measurement in DMF showed that the complex was non electrolyte (Table 3).

G_2: The light green complex (G_2) in chloroform exhibited bands at 12738, 14705, 26315 and 33112 cm^{-1}, which are assigned to $^3A_2g \rightarrow {}^3T_2g_{(F)}$, $^3A_2g \rightarrow {}^3T_1g_{(F)}$, $^3A_2g \rightarrow {}^3T_1g_{(P)}$ and (L) → Ni(II) transition, respectively. Data in Table 3 indicates octahedral geometry of Ni(II). The absence of any band below 10.000 cm^{-1} eliminates the possibility of tetrahedral environment in this complex. The different ligand field parameters (B^-, ν_1, Dq and β) have been calculated using Tanabe-Sugano diagram for d^8 system and found to be 490, 10976, 1097.6 and 0.43, respectively. The β value is found to be less than 1.0, indicating that the (Ni-L) bond is covalent. Magnetic moment of solid complex showed a higher orbital contribution. Conductivity measurement in DMF showed that the complex was non-ionic (Table 3).

G_3: The measured magnetic moment was 1.92 B.M. This show the Cu(II) ion it's dark green complex is typical of d^9 system. Electronic spectrum in chloroform shows one broad band at 14084 cm^{-1}, which corresponds to $^2B_{1g} \rightarrow {}^2A_{1g}$ transition, and a shoulder at 25773 cm^{-1}, which is assigned to $^2B_1g \rightarrow {}^2B_2g + {}^2Eg$ transition. The position of these bands is in a good agreement with that reported for highly distorted octahedral geometry. Conductivity measurement in DMF showed that the complex was highly ionic (Table 3).

The two complexes (**G_4**) and (**G_5**) were colorless in chloroform solution, so that no (d-d) transition can be expected in the visible region, as well as were diamagnetic as expected for d^{10} ions. The conductivity measurements indicate ionic behavior of the complexes (Table 3).

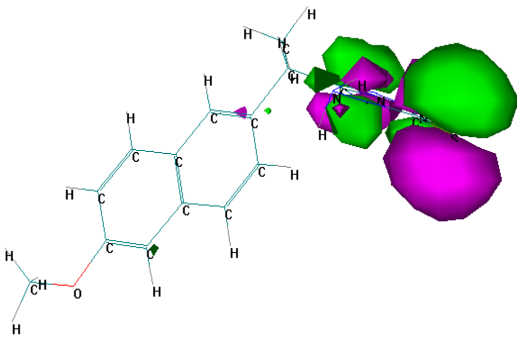
Table 3: Electronic spectra ($CHCl_3$), magnetic moment (B.M) and conductance in (DMF) for ligand and complexes

Symb.	Maximum absorption υ_{max} (cm^{-1})	Band assignment	10 Dq	Molar cond. S.cm^2.mol^{-1}	µeff. B. M.	Suggested geometry
(G_1)	6886.5 (Cal.)	$^4T_1g \rightarrow {}^4T_2g_{(F)}$	9337.6	11.65	4.03	Oh
	15174	$^4T_1g \rightarrow {}^4A_2g_{(F)}$				
	19157	$^4T_1g \rightarrow {}^4T_1g_{(P)}$				
(G_2)	10976, 12738 (Cal.)	$^3A_2g \rightarrow {}^3T_2g_{(F)}$	10976	16.09	3.02	Oh
	14705	$^3A_2g \rightarrow {}^3T_1g_{(F)}$				
	26315	$^3A_2g \rightarrow {}^3T_1g_{(P)}$				
	33112	C.T				
(G_3)	13850	$^2B_1g \rightarrow {}^2A_1g$	-	169.22	1.91	sp
	25641	$^2B_1g \rightarrow {}^2B_2g + {}^2Eg$				
(G_4)	30959	ILCT	-	165.86	0.0	Th
	38169					
	47169					
(G_5)	32573	ILCT	-	167.9	0.0	Th
	37037					
	43859					

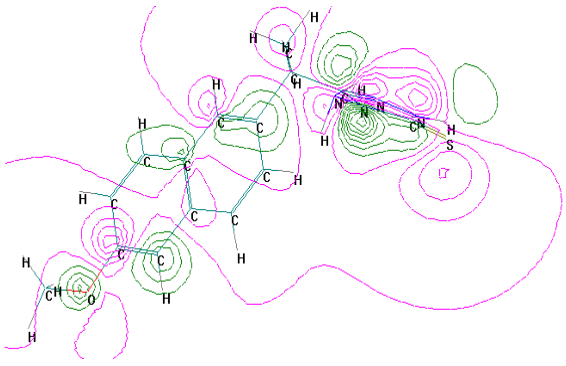
Theoretical studies of ligand (L) and its metal complexes

Electrostatic potentials

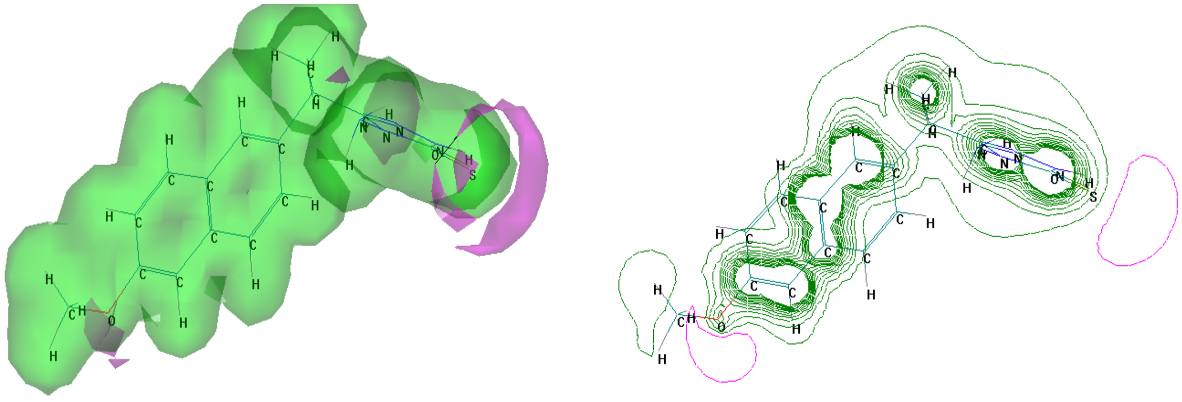
The electrostatic potential (E.P.) describes the interaction of energy of the molecular system with a positive point charge. E.P. is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule, where the electrostatic potential is strongly negative (electrophonic attack)[11,23]. The E.P of the free ligands (L) were calculated and plotted as 3D and 2D contour to investigate the reactive sites of the molecules (Fig. 3).



HOMO and LUMO in 3D for L



HOMO and LUMO in 2D for L



E.P. of L in 3D **E.P. of L in 2D**

Fig. 3: Electrostatic potential (HOMO and LUMO) as 3D and 2D contours for L

The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of sulfur and nitrogen atoms of free ligand (L).

Optimized energies

The conformations of the free ligand and its complexes obtained from the semi-empirical and molecular mechanics for calculations were fully reoptimized to estimate the heat of formation (ΔHf^o) and binding energy (ΔEb) by using the (PM3) method for free ligands (L) and its metal complexes (Table 4).

Table 4: Conformation energetic (in $KJ.mol^{-1}$) for ligand and its metal complexes

Comp.	**PM3**	
	ΔH^o_f	**ΔE_b**
L	355.132	-16260.116
(G_1)	-1569.29	-40387.661
(G_2)	-943.14	-39763.169
(G_3)	270.91	-33551.438
(G_4)	476.85	-32883.934
(G_5)	707.68	-32634.505

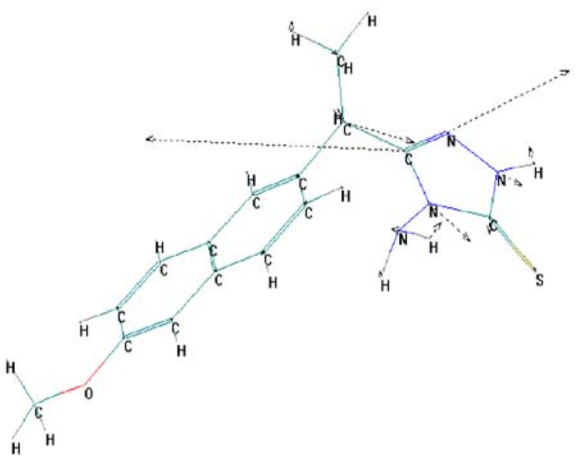
Optimized vibrational spectra for ligand (L) and its metal complexes

The vibrational spectra of the free ligand (L) and its metal complexes have been calculated (Tables 5, Figs. 4). The theoretically calculated wave numbers for this ligand showed some deviations from the experimental values. These deviations are generally acceptable in the theoretical calculations[24-26]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (L) and its metal complexes, (Table 5) and their respective experimental vibrational modes (Table 5, Figs. 4).

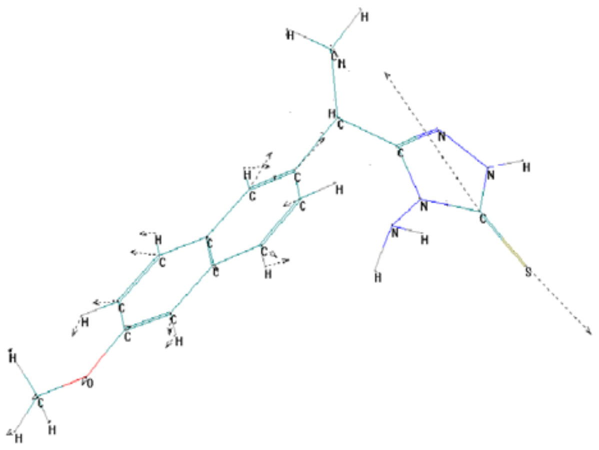
Table 5: Comparison of experimental and theoretical vibrational frequencies of the ligand and its metal complexes (cm^{-1})

Comp.	νC=S	νC=N	νNH$_2$as	νNH$_2$s	νNH	δNH + νC=N	νC=N + νC=S	νN-C-S	νCOO-
L	1041*	1645*	3265*	3211*	3441*	1595*	1380*	976, 654*	
	1044**	1650**	3368**	3250**	3409**	1451**	1392**	1018, 650**	
	0.28***	0.30***	3.15***	1.21***	-0.93***	-9.02***	0.86***	4.30, -0.61***	
(G$_1$)	1022*	1642*	3250*	3233*	3439*	1588*	1334*	970, 949*	1510,1302*
	1006**	1640**	3255**	3209**	3438**	1587**	1336**	972, 948**	1515,1309**
	-1.56***	0.12***	0.15***	-0.74***	-0.02***	-0.02***	0.12***	0.12, -0.02***	0.15,0.53***
(G$_2$)	1030*	1645*	3259*	3192*	3442*	1585*	1330*	947*	1511,1304*
	1031**	1649**	3228**	3213**	3438**	1609**	1329**	941**	1463,1309**
	0.02***	0.24***	-0.95***	0.65***	-0.11***	1.51***	-0.02***	-0.63***	-3.17,0.38***
(G$_3$)	1020*	1644*	3252*	3100*	3441*	1608*	1338*	972, 949*	
	1017**	1648**	3262**	3203**	3420**	1598**	1332**	989, 930**	
	-0.29***	0.24***	0.30***	3.32***	-0.61***	-0.62***	-0.44***	1.74, -2.00***	
(G$_4$)	1029*	1641*	3252*	3198*	3441*	1589*	1332*	949*	
	1036**	1675**	3355**	3228**	3429**	1527**	1334**	930**	
	0.68***	2.07***	3.16***	0.93***	-0.34***	-3.09***	0.15***	-2.00***	
(G$_5$)	1030*	1641*	3259*	3200*	3442*	1591*	1334*	949*	
	1025**	1692**	3384**	3244**	3427**	1422**	1368**	950**	
	-0.48***	3.10***	3.83***	1.37***	-0.43***	10.62***	2.54***	0.02***	

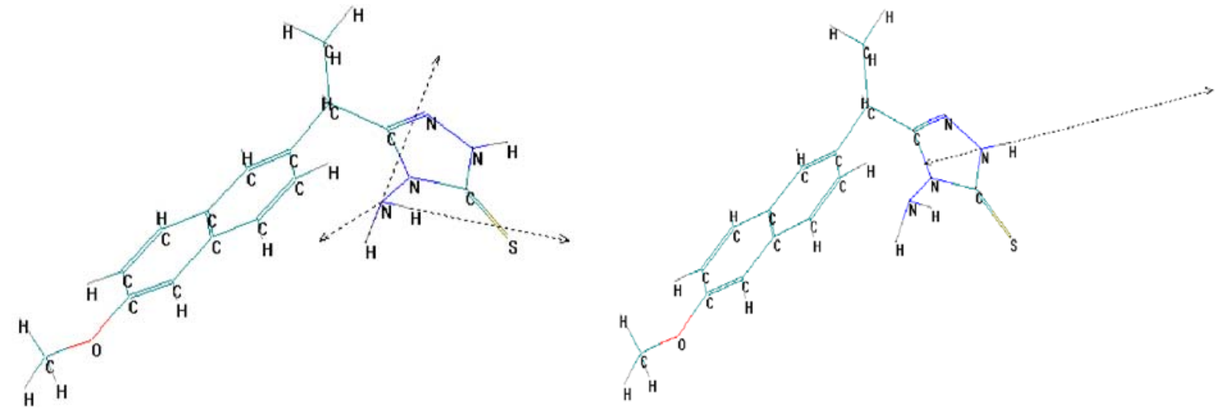
Where *Theoretical frequency, **Experimental frequency, ***Error % due to main difference in the experimental measurements and theoretical treatment of vibration spectrum.



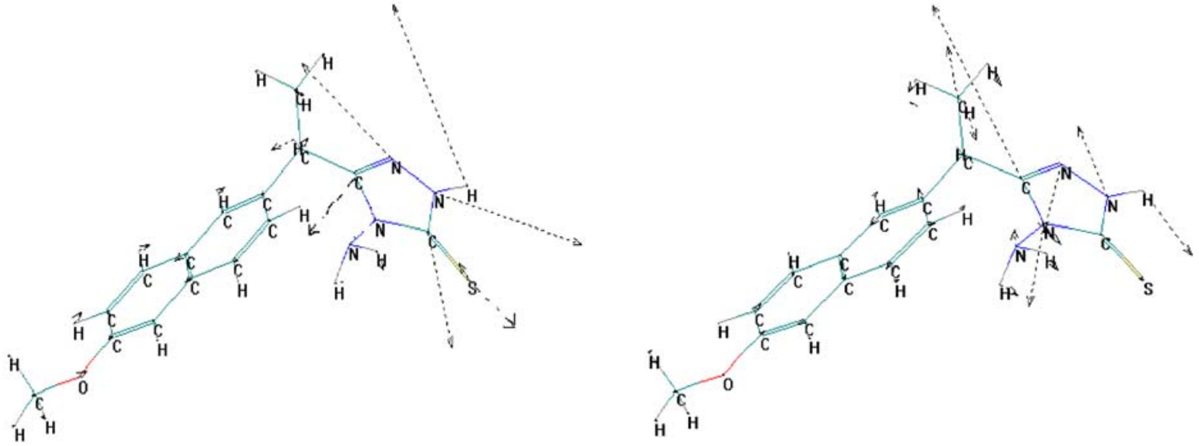
νC=N



νC=S



νNH$_2$ **νNH**



νC=N + νC=S **δNH + νC=N**

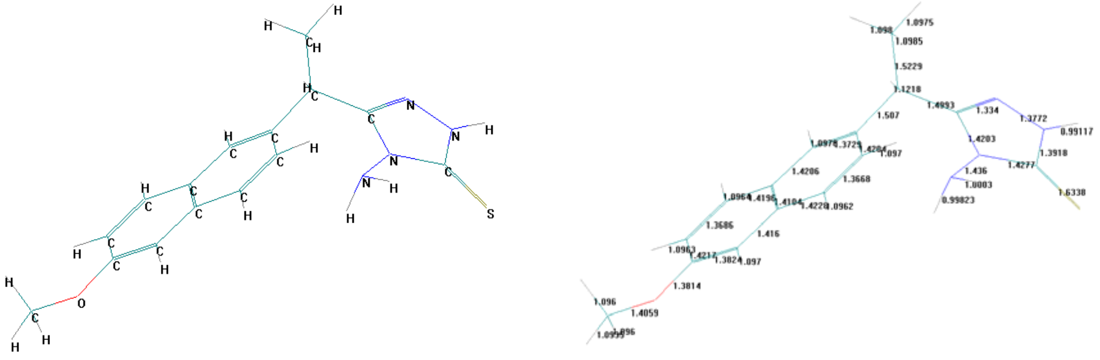
Fig. 4: The Calculated vibrational frequencies of (L)

Bond length measurements for the ligand and its metal complexes

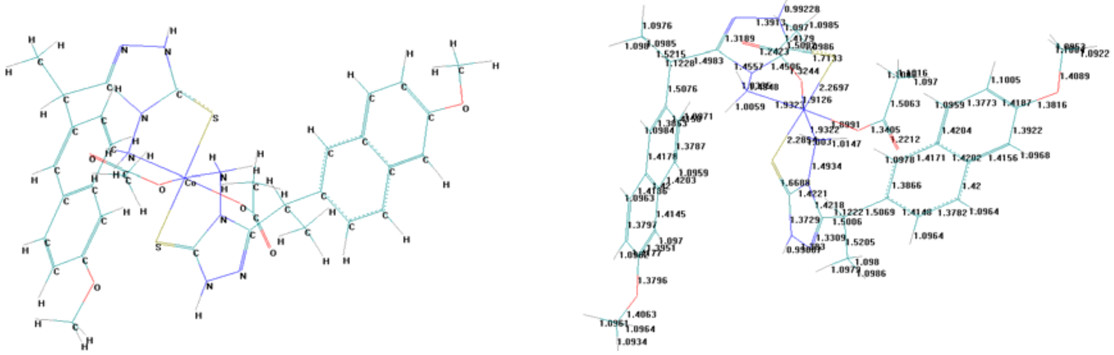
Calculation of parameters has been optimized and bond lengths of the free ligand and its metal complexes are reported (Table 6).

Table 6: Selected bond lengths (Å) for ligands and its metal complexes

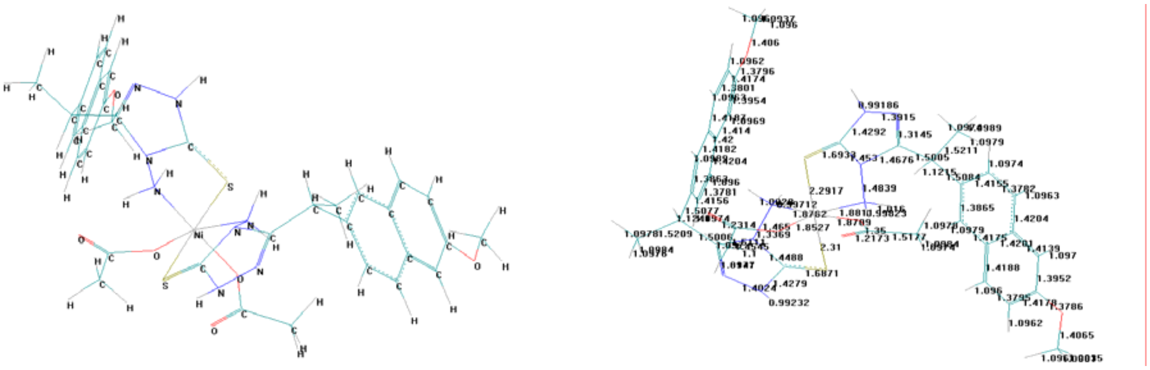
Compound	C=S	N-NH$_2$	M-S	M-N
L	1.633	1.436	-	-
(G$_1$)	1.646	1.465	2.679	1.854
(G$_2$)	1.674	1.937	2.288	1.937
(G$_3$)	1.765	1.877	2.174	1.863
(G$_4$)	1.658	1.566	2.204	1.891
(G$_5$)	1.739	1.475	2.396	1.968



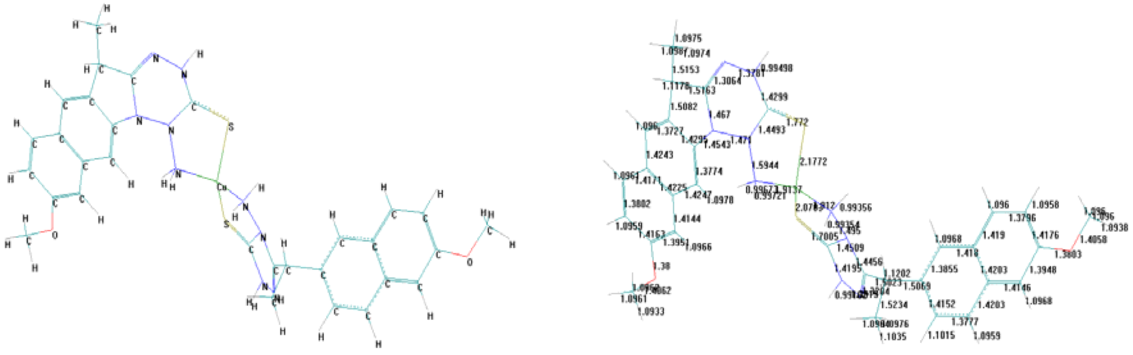
L



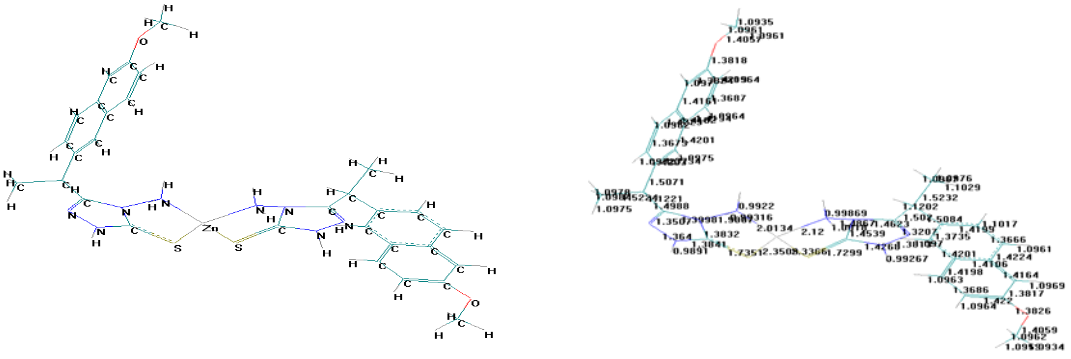
(G$_1$)



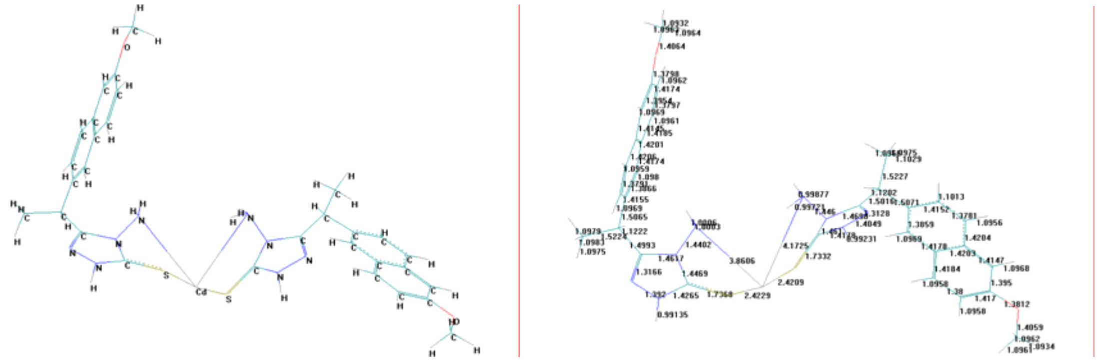
(G$_2$)



(G$_3$)

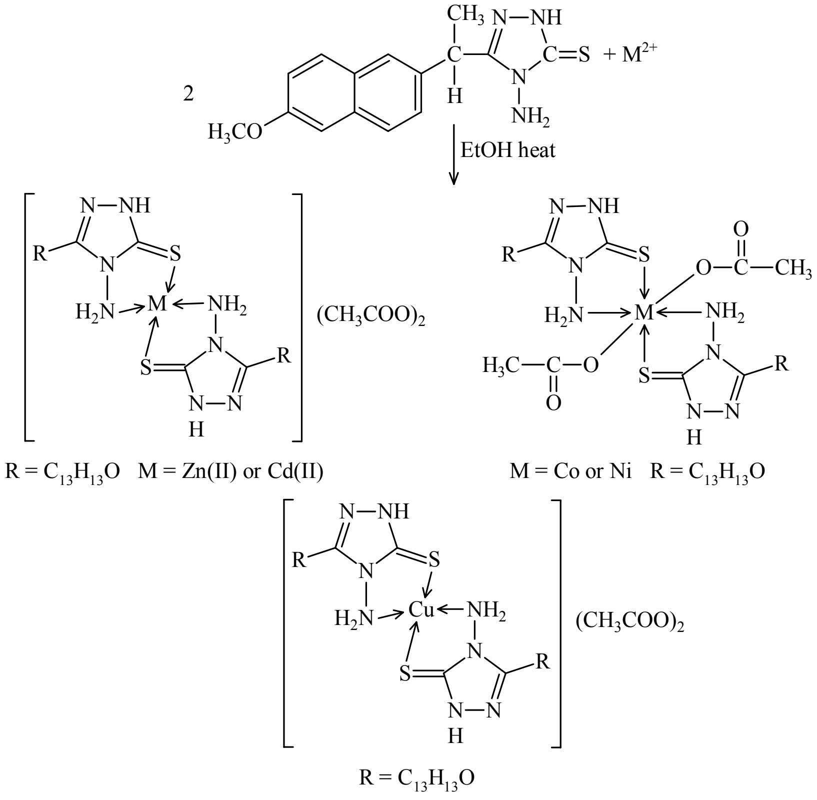


(G_4)



(G_5)

Fig. 5: Bond length of ligand and its metal complexes using hyperchem-8 program



R = $C_{13}H_{13}O$ M = Zn(II) or Cd(II)

M = Co or Ni R = $C_{13}H_{13}O$

R = $C_{13}H_{13}O$

Scheme 2: Synthesis of complexes (G_1-G_5)

CONCLUSION

This paper describes the synthesis and characterization 4-amino-5-(2-(6-methoxynaphthalen-2yl) piperidino)-1,2,4-triazole-3-thione (L) and its five complexes. The ligand acted as bidentate and coordinated to the metal atoms via the deprotonated carboxylate group. General structures of the complexes are shown in Fig. 2. The Co(II) and Ni(II) complexes probably show octahedral geometry, Cu(II) complex show square planar geometry, while Zn(II) and Cd(II) show tetrahedral geometry. The theoretical results by using (hyperchem-8) program agree with those found experimentally.

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