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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME TRANSITION METALS COMPLEXES DERIVED FROM BIS-PYRAZOLINE BASED LIGAND

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ABSTRACT A series of binuclear transition metal complexes with a general composition of (M2L(H2O)2Cl3 , [Zn2LCl3) where (M=Mn(II), Co(II), Ni(II) and Cu(II), L=.5,5'-(5-(tert-butyl)-2-hydroxy-1,3-phenylene)bis(3-methyl-4,5-dihydro-1H-pyrazole-1-carbothioamide) are reported herein. The new pyrazoline ligand was synthesized *via* the ring closure of 4,4'-(5-(tert-butyl)-2-hydroxy-1,3-phenylene)bis(but-3-en-2-one) in an alkaline solution of thiosemicarbazide after adjusting the stoichiometric ratios of the reactants. The new bis-2-pyrazoline was fully characterized by EIMS, NMR, FT-IR and elemental analyses upon completion of the TLC technique. The metal complexes of the new ligand were isolated in their solid state after adjusting the mole ratios (M:HL) 2:1 through the reaction of the metal chlorides with the ethanolic solution of the ligand (HL). The metal complexes were fully characterized by elemental analysis, molar conductance, molecular weight determination, FT-IR, UV-Visible and magnetic measurements. Molecular weight determination of these complexes indicate a binuclear nature. The octahedral geometry was confirmed on the basics of electronic spectra and magnetic measurement together with spectral and flame atomic absorption data. The zinc (II) complex was tetrahedral geometry with the formula Zn_2LCl_3. The complexes are non-electrolytic in nature negligible molar conductance. The anti-microbial activities of these derivatives have been studied by screening them against bacteria such as ***Staphylococcus aureus*** and ***Eschericheia Coli*** and fungi such as ***Aspergillus nidulece*** and ***Condida albicance*** by the serial dilution method.

Key words: Bis-2-pyrazoline ligands, Binuclear complexes of pyrazoline-based ligands, Biological activity of pyrazole complexes

1. INTRODUCTION

The coordination chemistry of bis-pyrazolederivatives is typically derived from the acyclic binucleating end-off compartment ligands (Chetna, K. Mohammad *et al*. 2014;Zuhal Ozdemir *et al* 2008). The binuclear complexes of pyrazole ligands besides being biologically, have considerable analytical, industrial and biochemical importance (Bogumiła, K. *et al* 2013,Attila, K. *et al*. 2007).The bidentate pyrazole ligands containing S, N and O-donor atoms were reported by many researchers due to the wide applications such as antitumor (Kratz F. *etal*, 2010), antifungal (Grotjahn D.B. *et al*, 2003, Sau, D. K. *et al* 2003),antiviral and insecticides agents (Grotjahn D.B. et al

2003). The use of transition metal complexes with azo dyes containing strong donor groups have also been used as spray reagent in chromatography.

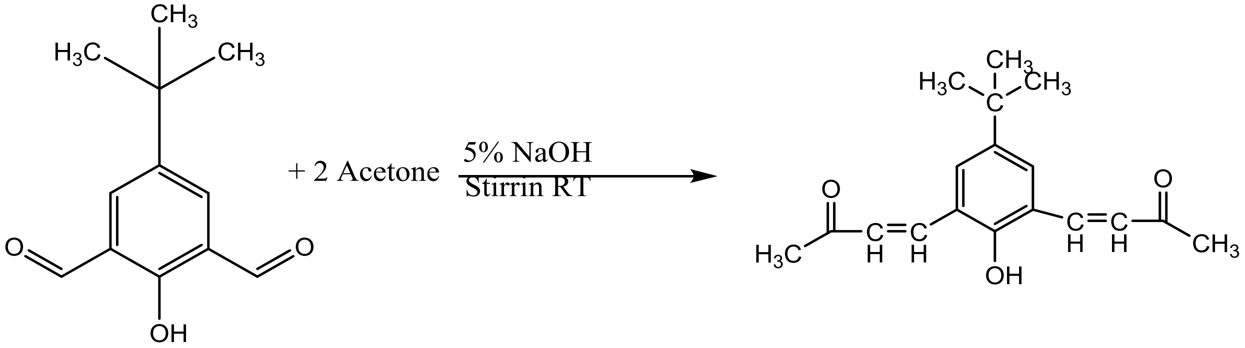
2. EXPERIMENTAL

All reagents and chemicals were commercially available and were used as received from the suppliers. The starting materials; 2,6-diformyl-4-tert-butylphenol, thiosemicarbazide (Merck), acetone 99 %, P ,$CuCl_2.2H_2O$, $ZnCl_2$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $MnCl_2.2H_2O$ were supplied from Sigma-Aldrich. All work were conducted in Chemistry Department, College of Science, Mustansiriyah University.

The melting points were determined in open capillaries and were uncorrected. The conductivity of the complexes were measured on Philips digital conductivity meter with dipping- type conductivity cell at 27 °C in 10^{-3} M solution in DMF. The vibration absorptions spectra were recorded on Shimadzu FT-IR spectrometer. The UV-Visible spectra of the ligand and its complexes were measured in the region (200–800) nm on Varian Cary 100 Conc. UV–Visible spectrometer. The NMR spectra of chalcone and ligand were measured in d6-DMSO solvent on Bruker 400 MHz NMR spectrometer at Faculty of Chemistry, Ghazi-Entab, University, Turkey. The magnetic moments were measured by Faraday's method on Sherwood magnetic balance at 300 °K temperature. The metal contents in the solid complexes were estimated by flame atomic absorption spectroscopy (FAAS) *via* standard methods, Table (1).

2.1 Synthesis of Chalcone

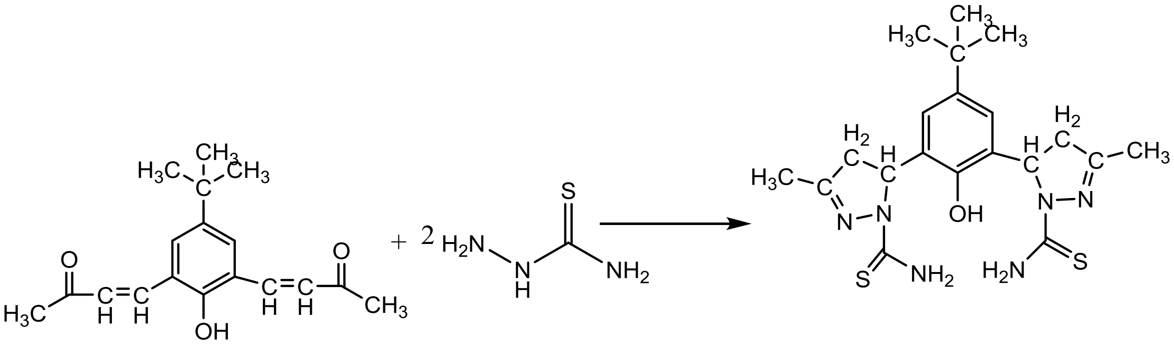
(1.65 g, 10 mmoles) of 2,6-diformyl-4-tert-butylphenol dissolved in (20 ml) methanol was added gradually to (20 mmoles, 10 ml) acetone followed by 5% NaOH solution . The reaction mixture was stirred at room temperature for three hours. A deep orange precipitate was formed, collected by filtration and were re-crystallized using chloroform to give deep-yellow crystals of the novel chalcone after keeping the precipitate overnight for 24 hours, Scheme(1).



Scheme 1. Synthesis of chalcone, (A).

2.2 Synthesis of 5,5'-(5-(tert-butyl)-2-hydroxy-1,3-phenylene)bis(3-methyl-4,5-dihydro-1H-pyrazole-1-carbothioamide

(0.286 g, 1mmole) of chalcone A and thiosemicarbazide (1.35 g,2.2 mmoles) in 1:2 molar ratio were mixed in 100 ml of hot methanol. The reaction mixture were refluxed for 30 minutes in a water bath before the pH of the solution was adjusted to slightly alkaline by using 10% NaOH solution (pH=8.0). The reaction mixture was left to reflux for about 12 hours. The precipitate was filtered off, dried in an oven then re-crystallized from hot methanol to afford the yellow crystals of the ligand, Scheme (2).



Scheme 2. Synthesis of ligand, HL

2.3 Synthesis of Metal Complexes

A mixtures (2 mmoles) of ethonolic solution of metal chlorides (0.34 g.$CuCl_2.2H_2O$),(0.257 g, $NiCl_2.6H_2O$), (0.44g $CoCl_2.6H_2O$), (0.375 gm, $MnCl_2.4H_2O$) and (0.36 gm of $ZnCl_2$) with (1 mmole, 0.433g gm) of ligand dissolved in (15 ml) hot methanol were refluxed for (1-3) hours and few drops of 5% NH_3 solution were added to the reaction mixture and maintain at pH $to \approx$6-7). The precipitate was filtered off, dried in *vacuum* in a desiccator over anhydrous calcium chloride for three hours, Table (1).

3. RESULTS AND DISCUSSION

3.1 Mass spectra

The mass spectrum of the chalcone (A) showed molecular ion at *m/z*=285 with 30 % relative abundance conforming the expected molecular formula of the enone (A), Figure (1). The observed peaks at 271 and 264 are assigned to the cleavage of the methyl and hydroxyl groups which confirmed the molecular formula and structure of chalcone (A). Figure 2 displays the mass spectrum of the free ligand (L) with variable peaks at 433, 415 assigned to the M^+ and M-OH of the ligand (Julio and P. Lucia, R. 2009). However, the low relative intensity of the molecular ion around *m/e*=433 resulted from the hard mass spectra technique in the gas phase.

3.2 NMR spectra

The ^1H NMR spectrum of the free ligand in d_6-DMSO showed absorptions around 11.84 and 9.84 ppm assigned to the nuclear spin of phenolic –OH and thioamide –H_2N-C=S protons respectively (Grotjahn D.B. *et al.* (2003) & Frankiine K. *et al.* 2008), in Figure (3). The peaks around (7.7-8.50) ppm are attributed to the nuclear spin of aromatic Ar-H protons whereas the peaks at 2.6 and 3.70 ppm are assigned to the aliphatic –CH_3 of tert-butyl group and vicinal and germinal protons of 2-pyrazoline ring respectively (Maurya *et al.* 2008). The ^{13}C NMR spectrum of the ligand were recorded in d_6-DMSO and the peaks observed at 15,18, 21 and 74.8 ppm are related to the aliphatic –CH_3 ,-C-CH_3, -CH_2-CH- of the 2-pyrazoline ring (Figure 4). The peaks around (160-153.2) ppm are assigned to aromatic carbon atoms and –C=N- of pyrazoline ring. The peaks at 188.9 and (169.2-162) ppm are associated with the nuclear spin of –C=S and –C-O moiety respectively [M. Goldstein *et al.* 1970 ; Krishan,C.H. *et al.* 1977).

3.3 Infrared Spectra

The IR spectrum of chalcone (A) in KBr disc exhibited strong absorption around (1650-1675) cm^{-1} which is attributed to vibration mode of carbonyl –C=O attached to –C=C in alpha-beta unsaturated compound (D.L Pavia *et al.* 2001). The absorptions around (1500-1600), 1275 and 2975 cm^{-1} are assigned to –C=C,-C-O and –C-H respectively (Tang H. *et al.* 2013). 2-pyrazoline ligand displayed new band around 1640, 1570, (3400-3180), 1080 and 1345 cm^{-1} associated with the –C=N-, -C=C-, NH_2 and –C=S groups, respectively, which confirmed the formation of 2-pyrazoline rings of bis-type (Julio, P. Lucia, R. 2009). The FT-IR spectra of all complexes showed lower frequencies in the region (1100-1310) cm^{-1} and (1657-1606) cm^{-1} of the thioamide and –C=N- of pyrazoline moiety, therefore is a strong evidence for the participation of the two moiety in binding with the metal ion (Jons, J. *et al.* 1993). The broad absorptions around (3498-3300) cm^{-1} revealed the hydrogen bonded –NH_2 of the thioamide moiety and coordinated water molecules in the inner-sphere of complexes. The weak bands around (586-534) and (405-432) cm^{-1} confirmed the formation of M-N and M-S bonds (Julio, P. Lucia, R (2009) & Nakamato, K.1997). The medium bands at around (2927-2750) cm^{-1} region in the complexes reveal that the phenolic –OH is coordinated to the metal ions, suggesting deprotonation during the formation of M-O-M bridge bonds (D.L Pavia *et al.* 2001). The high intensity bands around (1250-1245) cm^{-1} in the vicinity of (1325-1350) cm^{-1} are associated with the phenolic –C-O bonds.

3.4 Electronic spectra and magnetic musceptibility measurements

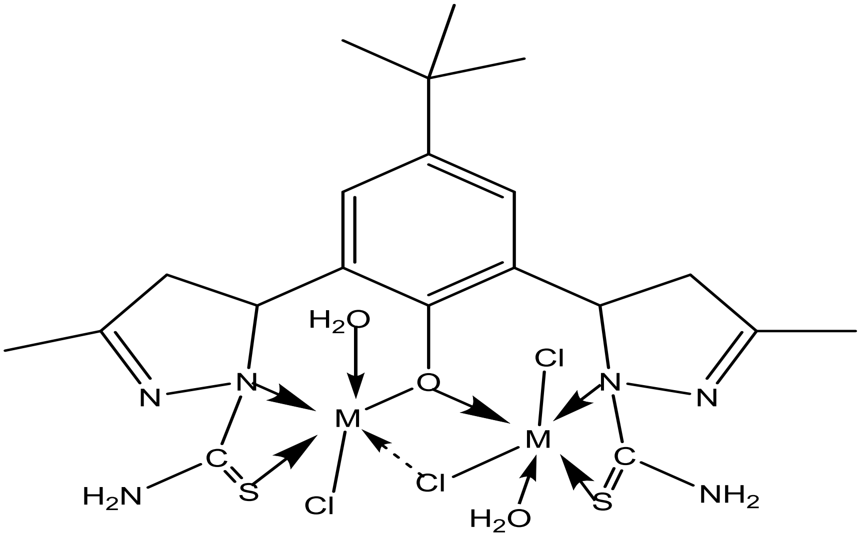
The electronic spectra of the free ligand, HL and its metal complexes were measured in the range (10,000-25,000) cm^{-1}. The dark brown solution of Mn (II) complex showed high intensity bands at around 28571 and 45455 cm^{-1} which are associated with the LMCT and ligand transitions, respectively. The weak absorption at 22222 cm^{-1} is clearly attributed to the $^6A_1g \rightarrow ^4T_1g(F)$ transition. However the observed magnetic moment of 4.75 BM of the Mn (II) complex was less than expected for an octahedral environment is due to the weak interactions of Mn-O-Mn and Mn-Cl-Mn bridges [Mane *et al.* 2002]. The cobalt (II) complex -exhibited three bands in the regions (10.000-30.000) cm^{-1} assigned to the $^4T_1g(F) \rightarrow ^4T_2g(F)$, $^4T_1g(F) \rightarrow ^4A_2g(F)$ and $^4T_1g(F) \rightarrow ^4T_1g(P)$ and confirms the octahedral geometry (Elzbieta ,B. *et al.* 2007). The proposed geometry is further confirmed by the weak anti ferromagnetic behavior in the range of 3.89 B.M. due to the Co-O-Co and Co-Cl-Co bridges bonds (Lever, A.B. 1994).The electronic spectra of Ni (II) complex displayed three bands in the region of 13.000, 19.700 and 25,300 cm^{-1} which are assigned to the $^{3}A_{2}g(F)\rightarrow{}^{3}T_{2}g(F)$,$^{3}T_{12}g(F)$ and $^{3}T_{1}g(P)$ transitions, respectively, suggesting an octahedral environment around the nickel (II) ion (R.L.Carlin *et al*. 1997). The magnetic moment of nickel (II) complex is 2.80 BM which is a strong evidence for the octahedral environment around the Ni(II) ion (Syamal and Maurya, (1986) & Stapathy *et al*. 1991). Furthermore, the olive solution of copper (II) complex in DMF showed two bands in the region (13.800- 28.600) cm^{-1} which are consistent with the $^{2}Eg\rightarrow{}^{2}T_{2}g$ and LMCT transitions, respectively, which confirms the distorted octahedral geometry. Further evidence for the weak anti ferromagnetic properties and metal-phenoxy and metal-chloro bridges was investigated from the diamagnetic character of the copper (II) complex which shows zero magnetic susceptibility (Lever, A.B. (1994) & Satish, M.A. 2007). However the molar conductance values of complexes in DMSO in the range (18-20) ohm-1.cm2.mole-1 indicate the neutral behavior of all complexes (Jerry, W.J. 1994).

3.5 Antimicrobial Activity

The obtained inhibition zones (mm) values of the 2-pyrazoline ligand and its metal (II) complexes in 20 ppm concentration are recorded by the diffusion method (Grotjahn D.B. *et al*. 2003)**.**The activity of the precursor complexes is listed in parenthesis. Like their precursor complexes, the antibacterial activity of the ligand was been tested against two fungi, namely the ***Aspergillus nidulence*** and ***Candida albicance*** and two bacteria namely the ***staphylococcus aureus*** and ***Escherichia coli***. The values suggest that all the metal complexes were more biologically active compared to the ligands. The observed activities showed that copper (II) complex has the greatest activity compared to the other complexes. The free bis-pyrazoline exhibited low inhibition zones due to the high polarity in DMSO which lessen their ability to cross the lipo layer of the bacteria and fungi cells (Grotjahn D.B. et al. 2003; Frankiine K. *et al*.2008). The *Ciproflaxin* was used as standard antibiotic drug as a comparison for the activity of the complexes solutions of 20 ppm.

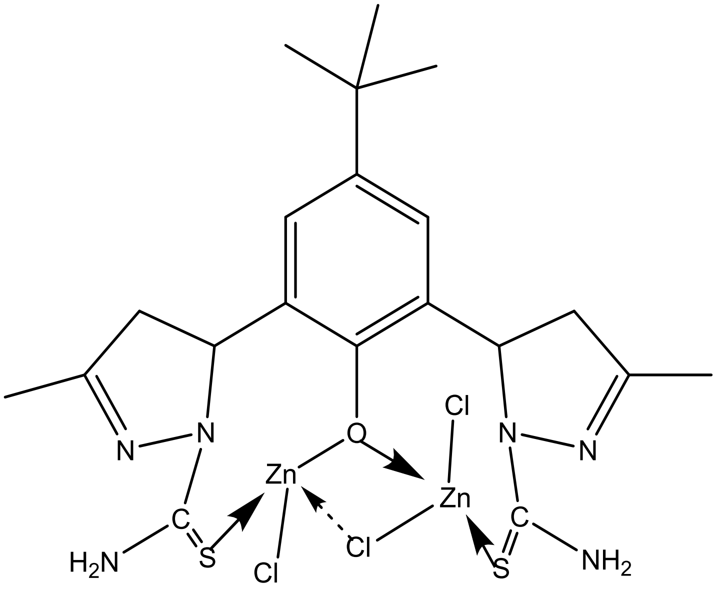
4. CONCLUSIONS

According to the data obtained from the elemental analyses, FT-IR spectra and magnetic moments, the octahedral environment was confirmed around the manganese (II), cobalt (II), nickel (II) and copper (II) ions, whereas, the tetrahedral geometry was proposed for the zinc (II) complex. The binuclear structure was approved *via* the anti ferromagnetic properties of the complexes at room temperature and the vibration absorptions of the metal-phenoxy-metal data. Furthermore, the results obtained from the IR spectra confirmed that the ligand was coordinated to the metal ions through the nitrogen atom of the pyrazoline ring –N1 , sulfur atom of the thioamide and oxygen of the phenolic –OH, after de-protonation forming a stable five-membered chelate ring, Scheme(3).



M=Mn(II),Co(II),Ni(II) and Cu(II)

Scheme 3. Octahedral geometry of the prepared [$M_2LCl_3(H_2O)_2$]complexes



Scheme 4. Tetrahedral geometry of [Zn_2LCl_3] complex

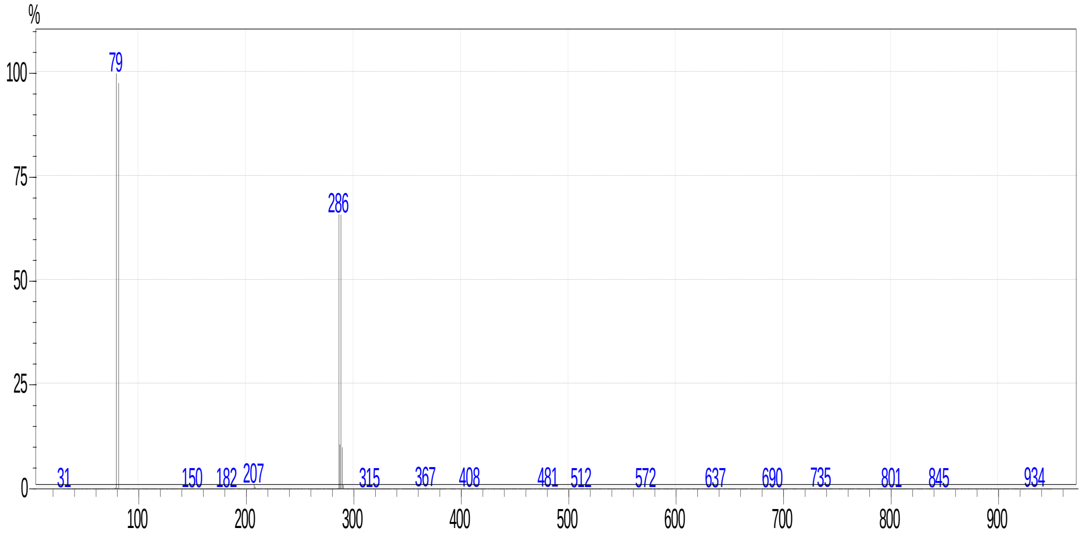


Figure 1. Mass spectrum of chalcone derivative ,A

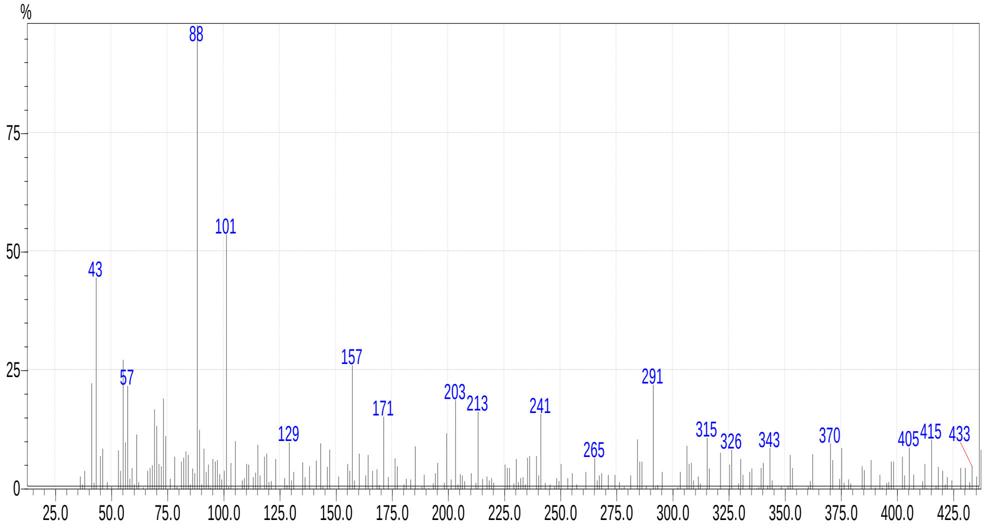


Figure 2. Mass spectrum of ligand, HL

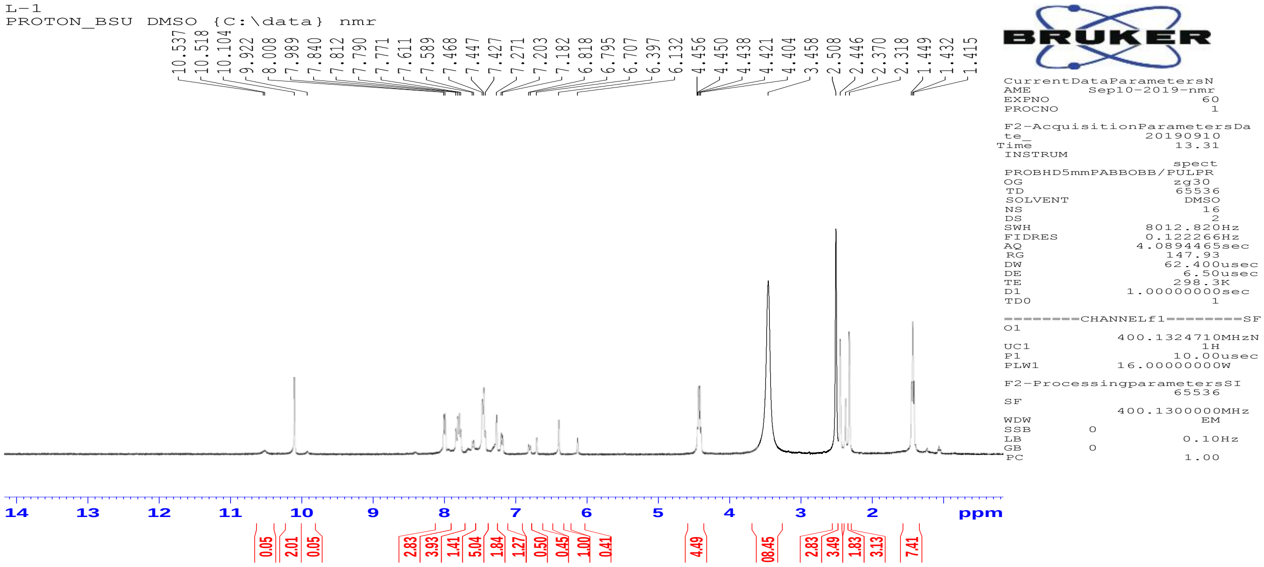


Figure 3. ^{1}H NMR spectrum of HL in DMSO-*d6* solvent

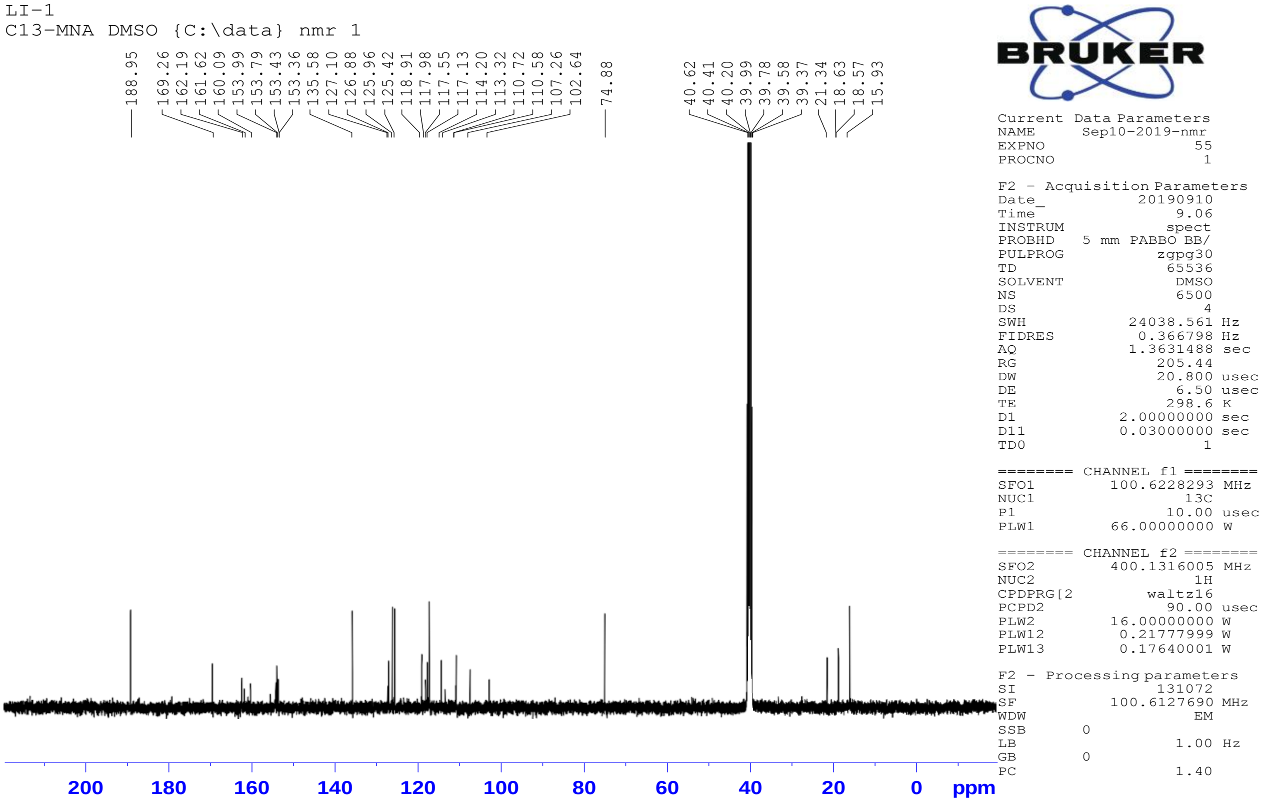


Figure 4. ^{13}C NMR spectrum of HL in DMSO-*d6* solvent

Table 1. Some physical properties and elemental analysis of the prepared complexes

Compound Color	Δ S.cm^2/mole	M.P ^{0}C	%Found % (Calculated)				
			C	H	N	S	M^a
[A] Deep yellow		210-212	74.66 (75.50)	6.88 (7.75)	-	-	-
HL Yellow		290-292	54.81 (55.54)	5.090 (6.52)	19.00 (19.42)	14.85 (13.87)	-
[MnL] Brown	20	303 Dec	36.50 (35.87)	4.99 (4.22)	12.59 (13.11)	8.95 (7. 88)	16.07 (15.76)
[CoL] Green	18	287 Dec	35.01 (34.21)	4.90 (3.97)	12.24 (13.22)	9.25 (8.96)	17.05 (16.63)
[NiL] Green	15	327 Dec	32.94 (31.89)	4.53 (4.11)	11.54 (12.00)	8.79 (8.11)	16.11 (15.89)
[CuL] Olive	15	283 Dec	52.80 (52.00)	3.11 (2.80)	16.44 (17.11)	11.08 (11.65)	15.78 (16.45)
[ZnL] Pale yellow	20	317 Dec	35.92 (34.81)	4.07 (3.68)	12.57 (13.30)	9.54 (8.88)	19.53 (18.77)

a=analyses of %M by flame atomic absorption spectroscopy (FAAS), Dec.=Decomposed

Table 2. I.R. Spectral bands of ligand and their metal complexes

Compound	VC=0	VC=N	V-NH	V-OH, -C-O	VM-N	VM-S
A	1650,1675(s)		3180(m)	3450(br)		
HL	-	1640(s)	-	3400(m), 1250(s)	-	-
[MnL]	-	1625(s)	3100(m)	3550(m), 1117(s)	515(m)	400(m)
[CoL]	-	1635(s)	3110(m)	3555(m), 1271(s)	490(m)	390(m)
[NiL]	-	1657(s)	3390(br)	3598(br), 1277(sh)	586(w)	405(w)
[CuL]	-	1633(s)	3175(br)	3540(br), 1266(s)	545(m)	435(w)
[ZnL]	-	1662(s)	3228(m)	3431(m), 1269(s)	503(w)	405(w)

br=broad, m=medium, s=strong and sh=shoulder

Table 3. Wave length, Magnetic Susceptibility and molar extinction coefficient for DMF solution of solid complexes

Compounds	**Molar Conc.**	**nmλ**	**ε_o L.mol^{-1} cm^{-1}**	**Assignment**	**μ_{eff}**
[HL]	1x10^{-3}	225	28900	$\pi \rightarrow \pi^*$	-
		315	30700	INCT	
[MnL]	1x10^{-3}	399	1500	$^{6}A_{1}g \rightarrow {}^{4}T_{1}g(F)$	4.75
		283	1.640	MLCT	
		240	3.467	$\pi \rightarrow \pi^*$	
[CoL]	1x10^{-3}	690	1600	$^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{2}g_{(F)}$	3.89
		570	700	$^{4}T_{1}g_{(F)} \rightarrow {}^{4}A_{2}g_{(F)}$	
		395	1080	$^{4}T_{1}g_{(F)} \rightarrow {}^{4}T_{1}g_{(P)}$	
		270	12700	LMCT	
				$\pi \rightarrow \pi^*$	

[NiL]	$1x10^{-4}$	750	555	$^3A_2g\rightarrow{}^3T_2g$	
		550	1200	$^3A_2g \rightarrow{}^3T_1g$	
		450	9040	$^3A_2g \rightarrow{}^3T_1g^{(P)}$	2.80
[CuL]	$1x10^{-4}$	830	120	$^2B_1g \rightarrow{}^2B_2g$	
		309	75	LMCT	
		287	2700	$\pi\rightarrow\pi^*$	0.0
[ZnL]	$1x10^{-4}$	370	10500	MLCT	0.00
		210	18950	$\pi\rightarrow\pi^*$	

LMCT and MLCT=Ligand to metal charge transfer or *vice-versa*

Table 4. Inhibition zones (mm) of HL and its complexes *via* diffusion method

Compound	**Bacteria**		**Fungi**	
	S.aureus	***E.coli***	***A.nidulence***	***C.albicance***
HL	12	20	10	11
[MnL]	15	27	13	14
[CoL]	22	21	16	18
[NiL]	20	22	18	15
[CuL]	28	30	20	22
[ZnL]	22	28	15	20
Ciproflaxin (20 ppm)	25	15	0	0

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Attila, K., Katalin M.,Vukadin M.,Zoran D. & Gyorgy, P. (2007). J. Organo-Metalic Chemistry 692m: 2582-2592.

Bogumiła, K., Krzysztof S., Katarzyna M., KamilaK., Malgorzata C., Bernhard K. & El-Zbieta B. (2013). Copper(II) complexes with derivatives of pyrazole as potential antioxidant enzyme mimics Med. Chem. Research 22:2395-2402.

Casas J.S., Castellano E.E., Ellena J., Garcıa-Tasende M.S., Luz Perez-Paralle M., Sanchez A., Sanchez-Gonzalez, A., Sordo, J.& Touceda A. (2008). New Pd(II) and Pt(II) complexes with N, Schelated pyrazolonate ligands: molecular and supramolecular structure and preliminary study of their in vitro antitumoral activity. J. Inorg. Biochem. 102 (1), 33–45.

Carlin , R.L. Vandryneveledt, A.J. (1997),. Magnetic properties of Transition Metal compounds Springer-verlag, New York PP.1-22.

D.L Pavia, D.L.Lampman, G.M., &G.S.Kriz.(2001). Introduction to Spectroscopy (3rd ed.).USA: Books/Cole Thomson Learning: pp.310-315.

Elzbieta, B. Magdalena, M. Bernhard, K. Keppler, Vladimir B., Arion, Grzegorz A. Julio, P. Lucia, R. (2009). Pyrazole Complexes and Supramolecular Chemistry. Eur.J.Inorg.Chem. 33:4913-4925.

Jerry W.J. (1971), Molar Conductivity measurements of Coordination Compounds in organic solvents,Coord.Chem.Reviews,7,81-122.

Krishan C.H., Mahapatra C.M.& Dash J.K. (1977). Synthesis and Spectroscopic Novel Transition Metals Complexes with Poly dentate 2-Pyrazoline Ligands. Inorg.Nucl. Chemistry 39**:**1253-1260.

Lever, A.B.P. (1994). Inorganic Electronic Spectroscopy, Elsevier Science Publisher Amsterdam, 155-160.

K.Nakamoto (1997), Spectroscopy and Structure of Metal Chelate Compounds, John Willey,New York pp.220-228.

Silverstein, R.M. (2003). Spectrometric Identification of Organic compound, 5thEdn. John Wiley,123-127.

Rossi G.,Rheingold A., Rideout M., Meyer C., Hemande Z.G. & Mejorado L. (2003). Bimetallic reactivity. Synthesis of bimetallic complexes containing a bis(phosphino)pyrazole ligand. J.Inorg.Chem.42:3347-3355.

Saleem K., Wani W.A., Haque A., Lone M.N. Hsieh M.F., Jairajpuri M.A.& Ali I., (2013). Synthesis, DNA binding, hemolysis assays and anticancer studies of copper(II), nickel(II) and iron(III) complexes of a pyrazoline-based ligand. Future Med. Chem. 5 (2), 135–146.

Sau D., Butcher K., Chudhuri R.J. & Saha, S. (2003). Antimicrobial activity of a series of thiosemicarbazones and their Zn^{II} and Pd^{II} complexes. Mol. Cell. Biochem. 253: 21-29**.**

Saka K., Tomistc Y., Ue T., Goshima K., Ohminat A.& M. Tsubomura (2002).

Structural and spectroscopic studies of binuclear Cu^{2+} and Co^{2+} complexes with an amide-based naphthalenophane Inorg. Chim. Acta. 297:64-71.

Saugata K., Atanu J,. Kinsuk D., Sangita R., Sudipta C., James A., Arnold L., Rheingold S. & Kumar K. (2011). Synthesis, crystal structure, spectroscopic and photoluminescence studies of manganese(II), cobalt(II), cadmium(II), zinc(II) and copper(II) complexes with a pyrazole derived Schiff base ligand. Polyhedron 30:2801-2808.

Sayed and N. Saglain, H. Bioorg.(2014). Synthesis and evaluation of pyrazolines bearing benzothiazole as anti-inflammatory agents. Med. Chemistry 23:5804-5812.

Stapathy, K.C. ,Panda, A.K. , Mishra, R. &Panda, I. (1991). Binuclear metal complexes. Part III. Complexes of 1-hydroxy-2, 3-dimethyl-5-carboxylato-1,4-diaza-1,3-pentadiene and 1-hydroxy-2,3-dimethyl-4(2′-carboxyphenyl)-1,4-diaza-1, 3-butadiene with bivalent transition metal ion complexes. Transition Metal Chemistry, 16, 410-412**.**

Satish, M.A. , Satisha, M.P., Vidyannand, K.R. (2007). Spectroscopic studies of bridged binuclear complexes of Co(II), Ni(II), Cu(II) and Zn(II). Transition Metal Chemistry 32: 81-87.

Syamal, A. , Maurya, R. (1986). Synthesis and characterization of nickel(II), cobalt(II), copper(II), manganese(II), zinc(II), zirconium(IV), dioxouranium(VI) and dioxomolybdenum(VI) complexes of a new Schiff base derived from salicylaldehyde and 5-methylpyrazole-3-carbohydrazide. Transition Metal Chemistry 11: 172-176.

Ting, H.Y.Silva, A.R.Shi & F.N. (2013). Six new 3d–4f heterometallic coordination polymers constructed from pyrazole-bridged $Cu^{II}Ln^{III}$ dinuclear units. Dalton Transaction 42:13997-1405.

Urszula K.&Marek R. (2007). Anion Separation with Metal-Organic Frameworks. Eur. J. Inorg. Chemistry 10:3728–3735.

Zuhal O., H. Burak K., Bulent G.,Unsal C. & Bilgin A. (2008). Synthesis and Biological Evaluation of a Series of Substituted Pyrazolo[3,4-*d*]-1,2,3-triazoles and Pyrazolo[3,4-*d*]oxazoles. Arch. Pharm. Chemistry 341: 701-707.