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Synthesis and Structural studies of Novel Macro cyclic Ligand Type N_2S_3 Donor atoms and Its Complexes with Some Transition Metals

MahmoudN. Al-jibouri ,TaghreedM.Musa[1], ,Enas Z.Mohammad
[1]Department of Chemistry, College of Science, Al-Mustansiriyah University
Corresponding author e-mail: mahmoudnajim71@yahoo.com, taghreedmohya@yahoo.com, and dr.wathiq@ yahoo.com

Abstract

A new pentdentate potential ligand HL was prepared by condensation reaction of 2-mercapto-5-methyl-benzene -1,3-dicarboaldahyde II with 1,2–diaminoethylsulfide–1,2–dichloroethene I in presence of methanol as a solvent .The new derivative (HL) was identified on the basis of microelmental analysis, (C.H.N.S), ^{1}HNMR, ^{13}CNMR ,FT- IR and UV-Vis spectroscopies. (HL) has been used as chelating ligand to prepare a new series of first row transition element complexes at pH (6-9) range. The colored solid complexes were isolated and characterized on the basis of (C.H.N.S)elemental analyses, UV-Vis, FT.IR spectroscopy ,as well as the proton and carbon-13 NMR for Zn,Cd and Hg(II) complexes were recorded to investigate the stereochemistry of the prepared complexes.The results obtained from elemental , spectral data and magnetic susceptibility revealed that all complexes were octahedral geometries of the general formula ,$[MLCl]Cl_n$, n=1 for Cr^{III}, Fe^{III} and n=0 for Mn^{II}, Co^{II} ,Ni^{II} and Cu^{II} in contrast Zn^{II}, Cd^{II} and Hg^{II} complexes were octahedral of electrolytic behavior in 1:1 suggesting the formula $[ML(H_2O]Cl$, M= Zn^{II}, Cd^{II}, Hg^{II} .

Keywords -: metal complexes, structural study and polydentate ligands N_2S_3 system

1. Introduction

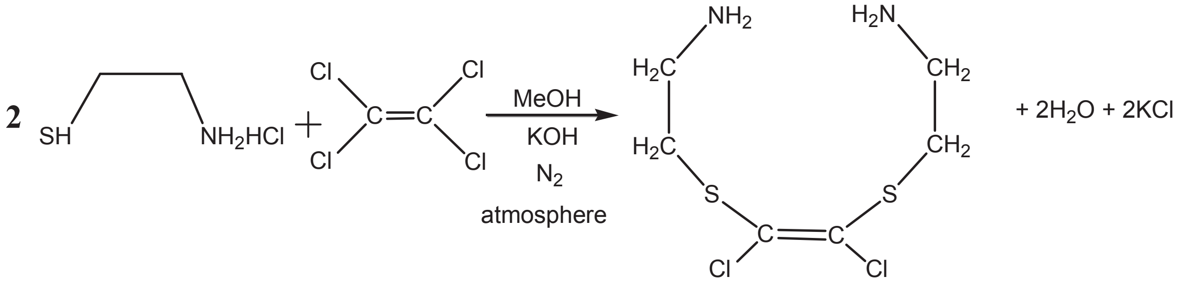
Synthesis and Characterization of the type of N_2S_3X-Fe of Iron and Zn containing Nitrile hydrates used in bioremediation of agriculture ,herbicidal and industrial waste water[1].Considerable attention has been paid to the coordination chemistry of Schiff base ligands containing nitrogen-sulfur donors towards transition metal ions, because these complexes can present many characteristics related biological systems containing metal ions in the same coordination environment[2].Thus it is a challenge for chemists to design appropriate macro cyclic frames with the purpose of synthesizing metal complexes with predetermined properties The ligands of the type N_2S_2, $N_2O_2$and N_2S_3 are considered to be good chelating agents because they involve both hard nitrogen atom and soft sulfur atoms [2] .The macro cyclic ligands of donating electrons of N_2S_2 systems have received much attention for further studies because they provide an interesting series of ligands whose properties can be greatly modified by introducing different organic groups[3]. As a consequence, unique solvatochromic properties have been observed for certain N2S3 molecules. Various electron donors, such as thiadiazole,oxadiazole and benzo-thiadiazole have been used for the design and synthesis of various coordinated compounds [4-5].The (N2S2) ligands have been employing to prepare complexes of some stereo chemical as well as biological importance [6-8]. The increased thermodynamic stability of macro cyclic complexes over their linear analogous having the same number of chelate rings is known as a macro cyclic effect. The donor atoms are positioned to coordinate preferably five or six member chelate rings are formed with metal ion[9]. As an effort to improve bioavailability and pharmacological and toxicological properties of polydentate ligands of 2,6-diformyl-phenol derivatives, many authors focused their research on the synthesis, characterization and biological evaluation of a large amount of metal complexes with this family of organic compounds [10-12].Macro cyclic complexes of Mn(II), Co(II), Ni(II) and Cu(II) using macro cyclic ligand derived by the condensation of *trimethoprim* and diethyl phthalate have been prepared and

2. Experimental

Reagents were purchased from Fluka and Merck and Redial-Dehenge Chemical Company. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400) cm^{-1}. Electronic spectra of the prepared compounds were measured in the region 200nm in for 10^{-3} M solution in DMF at 25C° using Shimadzu 160 spectrophotometer, with 1.000 ± 0.001 cm matched quartz cell. ^{1}H, ^{13}C- NMR were acquired with BRUKER-400 spectrometer in DMSO-d6solvent. The NMR spectra were recorded at Mary Collage, University of London/ United Kingdom. Elemental microanalysis were performed on a (C.H.N) by using Elemental analyzers Perkin –Elmer-240B, while metal contents of the complexes were determined by atomic absorption type Shimadzu (A,A-670). The chloride contents for complexes were determined by using potentiometer titration method on (686-Swiss). Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3}M solutions of the samples in DMF using a PW9527 digital conductivity meter.The magnetic susceptibility measurements were recorded at 2980 K^0 on the solid states applying Faraday' s method using Bruker BM6 instrument.

2.1 Synthesis (1,2-diamino ethyl sulfide-1,2-dichloro ethane)[1]

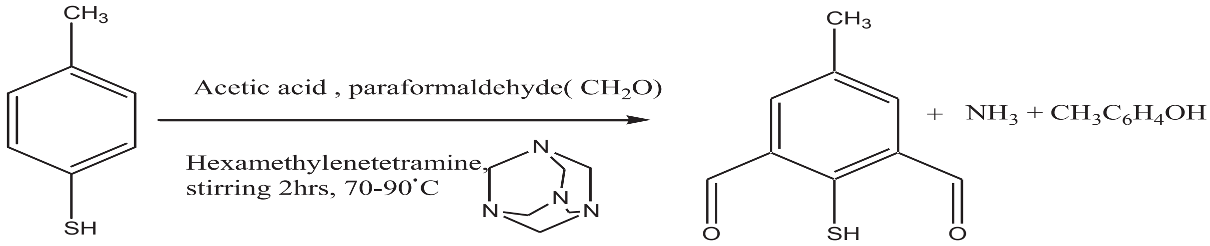
This compound was prepared, according to the method published in literature [14] Scheme (1).



Scheme (1) preparation route of compound [1]

2.2 Preparation of 2-Mercapto -5-methyl –benzene-1,3-dicarboaldahyde[II]

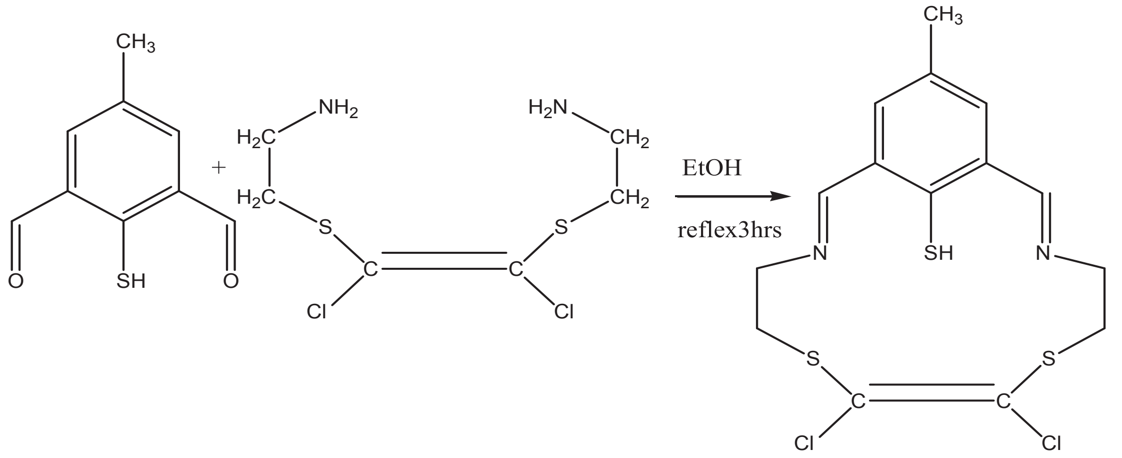
To a suspension of 4-methyl-1- mercabtobenzenel(12.4g, 0.01mole) in (60ml) acetic acid, hexamethylenetetramine (27.5g, 0.02 mole) and (5.99g, 0.02mole) of para formaldehyde were added. The mixture was allowed to stirred continuously until the light brown viscous solution was obtained and then heated to (70-90°C.) for two hrs. The reaction mixture was acidified after stirring with 10 ml of 98% H_2SO_4. The resulting solution was refluxed for further half-hr. Then the brown mixture was treated with (400mL) distilled water, followed a light yellow precipitate was formed, which was stored overnight at (4°C.). The yellow product was isolated by filtration and washed in small amount of cold methanol to afford (5.7g 31 %) m.p of light yellow (132–134°C) [Clark2004] Scheme (2).



Scheme (2) preparation of compound [II]

2.3 Preparation of ligand 1,2-dichloro-5,8-dimethyl-1,2-dithia-4,8-diaza–cyclotetradeca-1,5,8-triene [HL]

To compound (1) (5.0g, 0.022mol) in (30 ml) methanol,followed acidification by 10 drops of glacial acidic then (4gm, 0.022mol) of II compound in (15ml) methanol was added stepwise then refluxed the mixture on water bath under N2atmosphere for 4hours until, a brown precipitate was observed which filtered off and washed with ethanol, and then with petroleum ether to afford tap yellow crystals of [HL] ligand (64.60% yield), m.p=266-268C Scheme(3).



Scheme (3) preparation of the ligand

2.4 Synthesis of Metal complexes

(0.26 g, 0.001mol) of ($CrCl_3$. $6H_2O$) in (20 ml) methanol was added to(0.391g, 0.001mol)of [HL] ligand dissolved in methanolic potassium hydroxide to keep the pH of the solution for ≈8,then refluxed under nitrogen atmosphere for 3hours until a green solution has been turbid and after cooling to room temperature a green precipitate formed, filtered off, washed several times with 15ml of diethyl ether ,and dried under vacuum to offer (1.31 g, 65%) yield ,scheme(4).

A similar method was used to prepare Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}complexes except maintain the pH for ≈6-7 to form, Zn^{II}, Cd^{II} and Hg^{II} complexes, Table (1).

3. Result and Discussion

New polydentate (HL) ligand of N_2S_3 type scheme (3), has been prepared from condensation of compound [I] and [II]. The stoichiometric of the ligand and it's complexes were confirmed by their elemental analysis and the molar ratio method [M:L] at maximum absorption in the Uv-visible region Table(2,4). The ^1H and ^{13}C NMR in DMSO–d^6 solvent of the starting material [I] and [II], Table (5) displayed signals corresponding to the variants' proton and carbon nuclei respectively[15] for signal of C=C-S ^{13}C at(δ= 27 ppm) for C-S of compound [I].As well as the compound [II] exhibited sharp signal at (δ= 10.3 ppm)to equivalent 2H as signal to (C= O-H) [13-14] up on condensation the changing in positions and intensity of ^1H and ^{13}C NMR absorption reveal , the formation of (HL) ligand,Figure(1-2)

3.1 IR and NMR spectrum

In order to study the binding mode of the macrocyclic ligand (HL) to the mental ion in complexes the IR spectrum of the free ligand was compared with spectra of metal complexes.The IR spectrum of the (HL) ligand displays band in the region 1635-1596cm^{-1} as strong band, which assignable to imine group C=N [15]. As well as the weak absorption at 2320-2390cm^{-1} investigates the presence of S-H thiol group positioned in par position [16].Moreover the presence of medium absorptions at 900-1050cm^{-1} and 1020cm^{-1} confirms the C-Cl and C-S models of the prepared ligand, in KBr disk. In the spectrum of Schiff base complexes, the (υ C=N) mode of the ligand is formed to shift to lower wave number suggesting the coordination of the imine nitrogen atom to the central metal ion , in agreement with previous studies [15].The disappearance of weak absorptions inthe region in the spectrum of metal complexes confirms the deprotonation of S-H thiol group *via* coordination of sulphur atom (mercapto) to metal ion Furthermore, the new bands in the (395-415)cm^{-1} regions, supports the covalent bond of M-S [17]. The presence of medium absorptions at 900-1050cm^{-1} .The presence of S-H group positioned in Para position the forming of free ligand. Furthermore the presence of medium absorptions at 900-1050cm^{-1} and 1020cm^{-1} confirms the

C-Cl and C-S of the prepared ligand which appears in the lower frequencies region (395-415)cm^{-1} (M-S).As well as the metal complexes showed medium to weak absorption around (505-468))cm^{-1} which supports (M-N) band [18]. The water molecules coordinated toZn$^{(II}$, Cd^{II} and Hg^{II} complexes may be indicated from broad absorptions in the 3600-3450 cm^{-1} region[17].

The^{1}H NMR spectrum of the free ligand (HL) in DMSO-d^{6} solvent, Fig.(1) displays weak signal at (δ= 4.1 p pm) assigned to (N-C-H) protons and doublet absorptions at(7.8ppm) Ar-H moietyas well as the weak absorption of (δ= 2.95 ppm) for ^{1}H proton reveal the S-H group. The ^{1}H-NMR of Zn^{II}, Cd^{II} and Hg^{II} complexes in DMSO -d^{6} reveals the absence of S-H at (δ= 2.9 ppm) which suggests the coordination of SH group *via* deprotonation and the shifting in position and intensities of ^{13}C signal especially for C=N and C-S group (δ= 136.82- 48.13 ppm) for Zn^{II} and Hg$^{I\,I}$nvestigates the coordination of nitrogen atoms of C=N group to the metal ion [18-19].The resonance at(δ= 2.1 ppm,3H) attributed to methylene group.The^{13}C NMR spectrum of ligand (HL) shown in Fig.(2).The spectrum reveals resonances at (δ=166.54 ppm) and (δ=131.63 ppm) refer to the (H-C=N) and (C-S-H) carbons respectively.The resonances at (δ=129,118, 116 ppm) assigned to carbon atoms of aromatic ring. (C=C, C-C;C-H) .The chemical shifts at(δ=121.54 ppm) is due to (Cl-C=C-Cl).). The two resonance at (δ=31.0, 20.0 ppm,) is attributed to (C-S),(CH_3) carbon .

3-2 Electronic spectra, magnetic Moment and conductivity measurements for the metal Complexes:

Complexes of (HL) ligand with metals caused either batho chromic or hypso chromic shifts of the ligand bands,figure (2). The appearance of new medium and weak intensity peaks at higer wave lengths were observed either merged or slightly separated from the intra ligand (π→π*) . These peaks highly confirms the octahedral environment around Cr^{III} ion to charge transfers further bands with very low extinction coefficients appeared in the visible and new IR region. These bands were attributed to ligand field (d-d) transition [20] .The electronic spectra of (HL) ligand and it's metal complexes were recorded in absolute ethanol and DMF solution.

[(Cr^{III}LCl)Cl]complex

At room temperate, the magnetic moment of Cr(III) complex is (3.51 *BM*) corresponding to three unpaired electrons. The electronic spectrum of green solution of Cr^{III} complex in DMF displayed three peaks observed at 34482, 23201, and 16000cm$_{-1}$ which may be assigned to INCT, $^4A_2g(F)\rightarrow{}^4T_2g(F)$, $^4A_2g(F)\rightarrow{}^4T_2g(F)$, ^4Eg [21], absorptive in the ligand field andUv-region. These peaks highly confirm the octahedral environment around the chromium (III) ion.

[(Mn^{II}LCl)], [(Fe^{III}LCl)Cl]

The observed value of magnetic moment of Mn(II) complex at room temperature (4.95 BM) confirms the high-spin octahedral d^{5} configuration. The electronic spectrum of Mn^{II} complex in DMF solution shows three bands at 33333, 25641 and 21276cm^{-1} assignable to(L-F), INCT and$^6A_1g\rightarrow{}^4T_2g$ and$^6A_1g\rightarrow{}^4E_2g$ [22], these bands agrees with octahedral symmetry of Mn^{II} complex.As well as the brownish solution of Fe^{III}Complex in DMF Exhibits a weak intensity band at 18867 cm^{-1} which may be attributed to $^6A_2g\rightarrow{}^6T_2g$ [23] suggesting high-spin octahedral geometry around Fe$^{(III)}$, figure(3).

[(Co^{II}LCl)], [(Ni^{II}LCl)]

The magnetic moment of Co(II) complex and Ni(II) complexes are (2.95 *BM*)and (2,55*BM*) respectively,this reveals presence of three unpaired electrons for d^{7} configuration of Co(II) ion, and two unpaired electrons for high spin d^{8} of Ni(II) ion [23].The electronic spectra of Co^{II} complex in DMF solution displayed two weak intensity peaks at 16583cm^{-1}and14925cm^{-1} , which may be assigned to the spin allowed transitions $^4T_1g(F)\rightarrow{}^4T_2g(p)$, ($^4T_1g\rightarrow{}^4A_2g$ (F) and $^4T_1g(F)\rightarrow{}^4T1g(p)$ overlap with charge transfer of S' →Co ^{II} (C.T), LMCT. The position of such peaks suggests an octahedral geometry around Co(II).The electronic spectra of Ni ^{II} complex in DMF solution displayed four weak absorption peaks. The first one at 34722cm^{-1} was ascribed to ligand field and the second absorption peak at 31545cm $^{-1}$ may be attributed to charge C.T (M → L), while the third absorption peak at 20408cm^{-1}may be assigned to $^3A_2g\rightarrow{}^3T_1g$ transition of Ni ^{II} octahedral complexes[23] .

[(Cu^{II}LCl)] Complex

The electronic spectra of Cu^{II}complex in DMF solution displayed four weak absorption peaks. The first at 34722cm^{-1} refers to L.F which was shifted to high frequency when it comparison with that of free ligand. The second absorption peak at 31545cm $^{-1}$ was attributed to charge C.T (M → L), while the third a absorption peak at 20408cm^{-1} assigned to (d-d) transition electronic transition type ($^3A_2g\rightarrow{}^3T_1g(F)$ respectively which are a good agreement with Ni^{II} octahedral complexes 15384The electronic spectrum of Cu^{II} complex in DMF solution show bands at 700nm (14285), (530)nm, (18720cm^{-1}) and 440 nm (22727cm^{-1}). These peak may be assigned to the $^{2}B_{1}g \rightarrow {}^{2}B_{2}g$, $^{2}B_{1}g \rightarrow {}^{2}A_{1}g$ and change transfer transitions respectively. The position of last peak at 15384cm^{-1} and 1.94*B.M* confirms the distorted octahedral Cu^{II} complex

Zinc (II) cadmium (II) and mercury (II) complexes

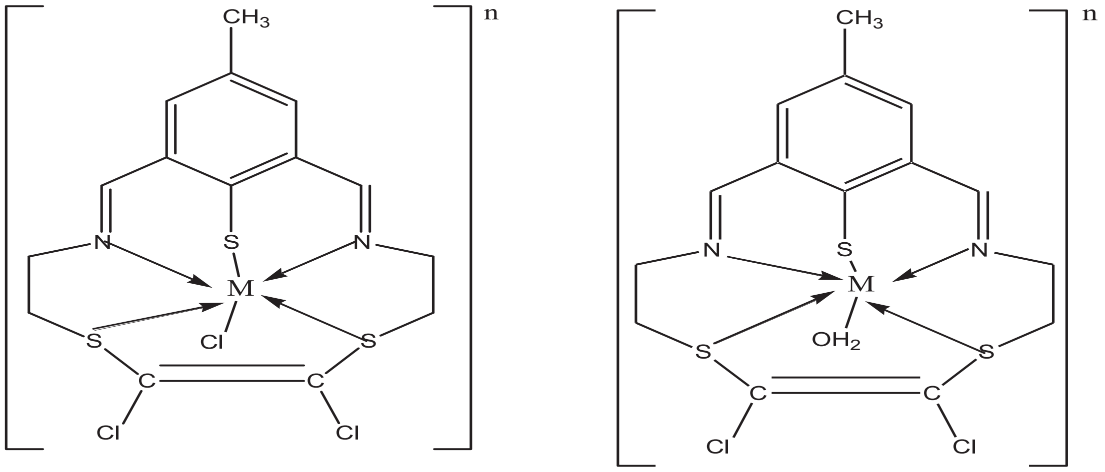
The electronic spectrum of Zn ^{II}, Cd^{II}andHg^{II}complexes exhibited bands related to the ligand (L-F), transitions, which appeared at280nm (35714cm^{-1}) and 360nm (27777cm^{-1}) respectively. No ligand filed transitions are observed because of filled d orbital. Since the d^{10} configuration affords no crystal filed stabilization, the stereochemistry depends on size and polarization power of the M^{II}action, and the steric requirement of the ligand [24].The other data of micro analyses,NMR. andIR.spectra proved the expected structures of such diamagnetic complexes[25].

3.3-The molar conductance:

All the metal (II) complexes in (DMSO) 10^{-3}M solutions 298^{0}K (table-5)exhibited non-electrolytic properties and the value of molar conductance of Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} electronic in DMSO fall in the(9 - 37) ohm^{-1}.cm^{2}ml^{-1} indicated their non-electrolytic nature[23],while the complexes[Cr^{III}(L)Cl], [Fe^{III}(L)Cl], [ML(H_2O]Cl, M =Zn^{II}, Cd^{II}, Hg^{II} showed conduct metric properties 1:1 ratio of the range 60-78 S.cm^{2}ml^{-1} there data investigate the proposed formula showed in recent paper [26-27] .

4. Conclusion

In this paper we reported the synthesis and characterization of novel macrocyicalic ligand [1,2-dichloro-5,8-dimethyl-1,2-dithia-4,8-diaza–cyclotetradeca-1,5,8-triene] derived from the reaction of [1] [1,2-diamino ethyl sulfide-1,2-dichloro ethene] with [2] [2-Mercapto -5-methyl –benzene- 1,3-dicarboaldahyde] and it's complexes with Cr(III),Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II). (HL) has been used as chelating ligand to prepare a new series of first row transition element complexes. The colored solid complexes were isolated and characterized on the basis of (C.H.N.S), UV-Vis, FT.IR spectroscopy as well as magnetic moment (μ_{eff}) and molar conductance of their solution (10^{-3} M) in DMSO. The results obtained for elemental and spectral technique revealed that all complexes were octahedral geometric of the general formula ,[MLCl]Cl$_{n}$, n=1 for Cr^{III}, Fe^{III} and n=0 for Mn^{II}, Co^{II} ,Ni^{II}andCu^{II} in contrast Zn^{II}, Cd^{II} and Hg^{II} complexes were octahedral of electrolytic behavior in 1:1 in suggested formula [ML(H_2O]Cl , M= Zn^{II}, Cd^{II}, Hg^{II}



M=Cr^{III}, Fe^{III}, n= +1
M=Mn^{II}, Ni^{II}, Cu^{II}, n=0

M=Zn^{II,} Cd^{II}, Hg^{II}, n=+1

Scheme(4):stereo chemical structures of the prepared complexes.

References

[1] Melson G.A. Coordination Chemistry of Macrocyclic Compounds; *Plenum Publishing Corp.* :New York, NY, USA(1979**).**

[2] Formanowskii A.A., Mikhura I.V. "Synthesis of Macrocyclic Compounds. In Macro -cyclic Compounds in Analytical Chemistry" Zolotov,Y.A., Ed.*Wiley-Interscience*: New York, NY,USA,; pp. 5-39(1997).

[3] Chartres J.D., Davies M.S., Lindoy L.F., Meehan G.V. and Wei G. Macrocyclic ligand design:The interaction of selected transition and post-transition metal ions with a 14-membered N2S2-donor macrocycle. *Inorg. Chem. Commun*., 9, 751-754D(**2006**).

[4] Guodong E., Arkady and W,Kelth, *Inorg. Chem*, 42, 873-877**(2003)**.

[5] Toman P.,Makrlik E. and VanuraP.A "combined experimental and theoretical study on the complexation of the ammonium ion with benzo-18-crown"*Monatsh.Chem.*,141,301-304 (**2010**).

[6] Hancock R. Molecular mechanics calculations and metal recognation. *Acc.Chem.Res.* , 23,253-257(**1990**).

[7] Shargh D.N. and Hosseini M.M."Ohaninan,T.Configurational and Conformational Proper -ties of 1,3,7,9-Tetraphospha-Cyclododeca-1,2,7,8- tetraene: An Ab Initio Study and NBO Analysis. Phosphorus Sulfur",183, 2410-2420(**2008**).

[8] Azizoglu A. and YildizC.B.Ring-opening mechanism of lithium bromosilacyclopropyli -denoids to silaallenes. Organometallic, 29, 6739- 6743**(2010)**.

[9] ZhengX.,WangX.,Yi S. , Wang N. and Peng Y. DFT study of the carbon- and nitrogen-pivot lariat crown ethers and their complexes with alkali metal cations: Na^+,K^+. *J. Comp. Chem.*, 30, 2674-2683(**2009**).

[10] Yuan,M.;Xueye,W.;Xin,J.;Ling,Y.;Cuihuan,R.DFT study for a seria of less-symmetrical crown ethers and their complexes with alkali metal cations.*Chin.J.Chem.*,28,1835-1843,pp.233-240 (**2010**).

[11] Kilbas B.; Azizoglu A. and BalciM.Edo "exo-configured cyclopropylidenes incorporated into the norbornadiene skeleton: Generation, rearrangement to allenes, and the effect of remote substituents on carbene stability". J.Org.Chem.,74,7075-7083(**2009**).

[12] Kurtaran R., Odabaşıoğlu S., Azizoğlu A., Kara H. and Atakol O. "Experimental and computational study on [2,6-bis(3,5-dimethyl-n-pyrazoyl)pyridine]-(dithiocyanato) mercury (II). Polyhedron" 26, 5069-5074(**2007**).

[13] Y.Goodman,D.C.,Buonomo, R.M.,Farmer, P.J.,Reibenspies,J.H. and Darensbourg, M.Y. ; *Inorg. Chem.Rev.,*35, 4029, **(1996)**.

[14] Odabasioglu, S.; Kurtaran, R.; Azizoglu, A.; Kara, H.;Oz,S.;Atakol, O.Experimental and computational study on [2,6-bis(3,5-dimethyl-N-pyrazolyl)pyridine]-(dithiocyanato)mercury (II). *Cent. Eur. J. Chem.*, 7, 402-409. **(2009**).

[15] Silverstein R, Webster F."spectra photometric Identification of Organic Compond" 6th ed., John Wiley and Son, New York(1998).

[16] Jun-ichi; NARASO; Murai,Shiro; Fujiwara, Eiichi; Tada, Hirokazu; Tomura, Masaaki; Yamashita , *Yoshiro Org. Lett.* **6**, 2007– 2010 (**2004**)

[17] Cheeseman G.W. H.; Cookson, R. F. Condensed Pyrazines. In The Chemistry of Heterocyclic Compounds; Vol. 35, Weissberger, A.; Taylor, E. C. series editors; John Wiley & Sons, Inc.: New York,; pp.78-111**(1979**)

[18] R.K.Bansal. Heterocyclic Chemistry,3^{rdEd},*New Age International(P)Limited*, New Delhi **(2002)**.

[19] A.D.Naik, S.M.Annigeri,U.B.Gangadharmath,V.K. Revankar,V.B.Mahale. *J.Mol. Struct.* , 616, 119, **(2002).**

[20] NakamatoK."Infrared spectra of Inorganic and coordination compound", John W. and Son, New York .

[21] W.Huang, S.Gou and Q. Meing, *Inorg, Chem.*,40,1712-1715(2001).

[22] Tisato F.,MazziBandoli, Cros G. , Darbieu M., Coulais, and Guirand,R.;*J,Chem.Soc . Dalton Trans.*,1302,(1991).

[23] U.Abram, J.A.MC.Cleverty and T.J.Meyer," Comprehensive Coordination Chemistry" Ed. Elsevier, 27, (2004).

[24] I.V.Jeary "Characterization of metal complexes via conductivity in organic Solvent, "(1971)

[25] Martin C.,HannahJ.,AndrewR.,Julia M. and Dilworth R. "Isolation and Crystal Structure of Novel by products observed during formation of macrocyclic , N2S2 ligand *Trans. Met. Chem.* 31.88, **(2006)**

[26] Satyanarayane D.N. "Electronic Absorption spectroscopy and Related Techniques Universities press, Hyderabad, (2001).

[27] W. Jerry "The Use of Conductivity measurements in Organic solvents for the Characterization of Coordination Compounds"*Coord,Chem.Reviews*(1971).

Table (1): physical properties of the prepared compounds and weight of metal chloride salt

Sympol of compound	Molecular formula	Yield%	colour	M.P.°C	Wt .of metal chloride(g)
compound[1]	$C_6H_{12}N_2S_2Cl_2$	88	Light yellow	141-143	-
compound[2]	$C_9H_8O_2S$	35	yellow	132-134	-
[HL]	$C_{15}H_{16}N_2S_3Cl_2$	64	Deep yellow	266-268	0. 391
C_1	$C_{15}H_{15}N_2S_3Cl_4$ Cr	53	dark green	290	0. 202
C_2	$C_{15}H_{15}N_2S_3Cl_3Mn$	64	Brown	270	0.198
C_3	$C_{15}H_{15}N_2S_3Cl_3Fe$	75	dark red	300	0.356
C_4	$C_{15}H_{15}N_2S_3Cl_3Co$	62	Brown	280	0.242
C_5	$C_{15}H_{15}N_2S_3Cl_3Ni$	50	Brown	290	0.236
C_6	$C_{15}H_{15}N_2S_3Cl_3Cu$	58	Brown	288	0.170
C_7	$C_{15}H_{17}N_2S_3Cl_3OZn$	60	Yellow white	280	0.136
C_8	$C_{15}H_{17}N_2S_3Cl_3OCd$	62	Yellow	260	0.230
C_9	$C_{15}H_{17}N_2S_3Cl_3OHg$	53	grey	286	0.271

Table (2): Result of elemental analysis and physical properties of [HL]

Compounds	M. wt			Found(Calcd)%			
		C%	H%	N%	S%	Cl%	Metal
$C_6H_{12}N_2S_2Cl_2$ [1]	247	28.20	4.01	12.19	23.91		-
		(29.15)	(4.89)	(11.33)	(25.94)	28.68)	-
$C_9H_8O_2S$ [2]	180	57.09	3.53	-	16.55		
		(59.98)	(4.47)	-	(17.79)	-	-
$C_{15}H_{16}Cl_2N_2S_3$ [HL]	391	45.21	3.20	7.86	22.31		
		(46.03)	(4.12)	(7.16)	(24.58)	(18.12)	-
[C_1]	513	33.07	2.14	6.23	16.83		9.04
		(35.1)	(2.95)	(5.46)	(18.21)	(27.63)	(10.13)
[C_2]	496	36.96	3.21	5.98	17.67		10.32
		(38.68)	(3.85)	(5..64)	(19.36)	(21.41)	(11.06)
[C_3]	381	35.08	2.99	5.93	1823.		(10.52)
		(37.40)	(3.14)	(5.82)	(19.97)	22.08	(11.59)
[C_4]	484	36.12	2.82	6.02	19.11	-	11.55
		(37.16)	(3.12)	(5.78)	(19.84)	(21.94)	(21.16)
[C_5]	484	36.15	2.59	5.99	18.12		23.11
		(37.18)	(3.12)	(5.78)	(19.85)	(21.95)	(24.47)
[C_6]	486	35.33	2.66	5.98			11.12
		(36.81)	(3.09)	(5.81)	(19.66)	(21.73)	(12.11)
[C_7]	509	35.05	2.99	5.90	17.43	-	12.11
		(35.38)	(3.36)	(5.50)	(19.53)	20.89)	(12.84)
[C_8]	556	32.95	2.11	5.79	15.99	-	19.08
		(33.47)	(3.08)	(5.04)	(17.29)	(19.12)	(20.21)
[C_9]	644	28.08	2.03	5.10	13.01	-	30.98
		(27.69)	(2.66)	(4.35)	(14.93)	(16.50)	(31.13)

Table (3): Infrared spectral data (wave number) cm^{-1} of the ligand [HL] and its complexes

Compound	υ(C=N)	υ(SH)	υ(C-H)	υ(C-S),υ(S-C-S)	υ(M–N)	υ(M-S)	υ(C=C)	Additional bands
[HL]	1643m	2390		1020m 640			1533	3003m υ(C–H) arom. 2900w υ(C–H) aliph
[C1]	1620	-	1082m	1033m 620	498m	418w	1540m	3000m υ(C–H) arom. 2970vw υ(C–H) aliph 1457w *
[C2]	1629	-	1060	1029 632	470	418	1540	
[C3]	1650	-	1082	1025 326	478	430	1521	
[C4]	1648s	-	1016m	1035 620	475	410	1505w	3090m(C–H) Ar 2930w(C–H) aliph 1490w *
[C5]	1635	-	1050	1019 628	486	418	1511	
[C6]	1639m	-	1050w	1029 634	550w	412w	1529w	3000m υ(C–H)Ar 2970vw υ(C–H) aliph 1440w *
[C7]	1633s	-	1015m	1036 619	490	418w	1551m	3050m υ(C–H)Ar 2900vw υ(C–H) aliph 1446w *
[C8]	1650m		1117s	1027m 637	479	405w	1534m	3010m(C–H) Ar 2940w (C–H) aliph 1488w *
[C9]	1640s		1122s	1020 630w	468	412w	1558w	3000m(C–H) Ar 2900w(C–H) aliph 1458w *

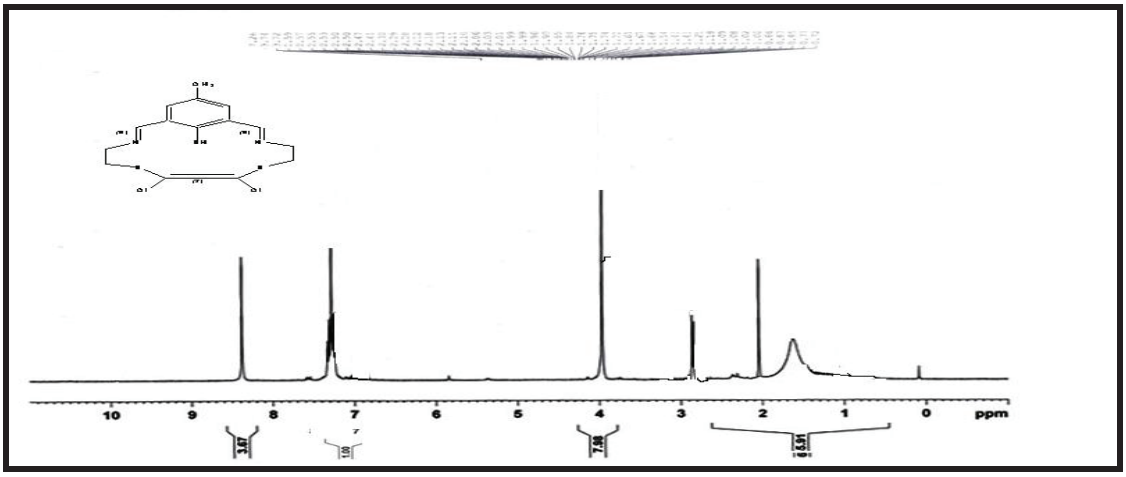
*=referred to bending of (C-N) bond as weak absorption,strong(s), broad(br), medium(m), (w) weak,

Table (4):^{1}H ^{13}C NMR Data for the ligand measured in DMSO- d^6 and chemical shift in ppm(δ)

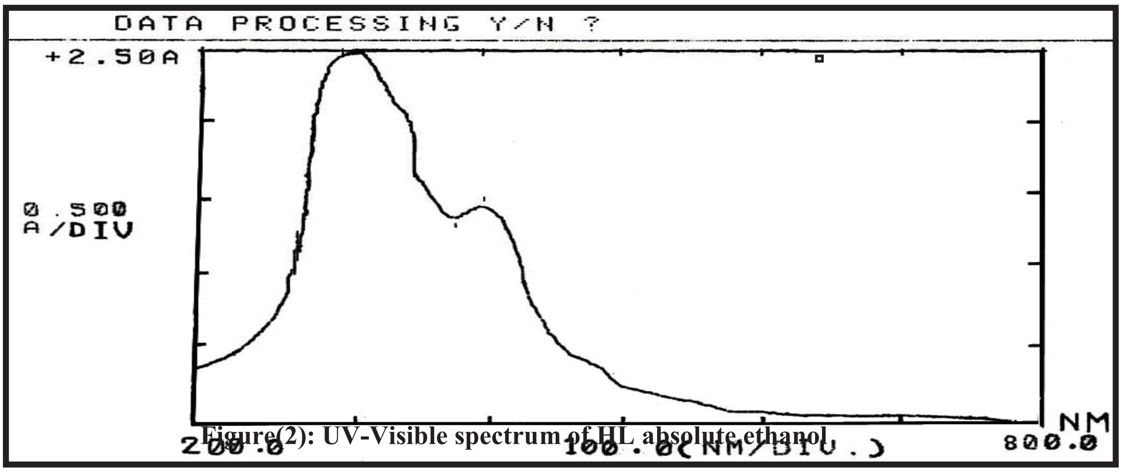
Compound	Funct. Group	δ_H(ppm)^b
[HL] ^{1}H ^{13}C	H-C=N ; Ar. C-H ; N-CH_2; S-CH_2 Aliphatic CH_3; C-S	8..30, (2H, S); (7.8, 7.1) (2H,S); 4.1, (2H, S); 2.95(2H, s) 2.1 (3H, S); 2.90 (1H,s)
	H-C=N ; Ar.(C=C, C-C;C-H) ; (C-SH); C-N Cl-C=C-Cl; S-C-H_2 , Aliphatic C--H_3	166.54 ; (129.118, 116) 131.63; 59.00 121.54 ; 31.26 20.20
C7 ^{1}H	H-C=N ; Ar. C-H ; N-CH_2; S-CH_2 Aliphatic CH_3	8.40 (2H,s); 7.7(2H,s) 3.9 (4H, s); 2.1 (4H, br) 1.7 (3H, br)
C8 ^{1}H	H-C=N ; Ar. C-H ; N-CH_2; S-CH_2 Aliphatic CH_3	8.10. (2H,s); 7.2 (2H,s) 3.8 (4H, br); 1.8 (4H, br) 1.3 (3H, br)
C9 ^{1}H	H-C=N ; Ar. C-H ; N-CH_2; S-CH_2 Aliphatic CH_3	8.50. (2H,s); 7.3 (2H,s) 3.8 (4H, br); 2.1 (4H, br) 1.5 (3H, br)

Table (5): Electronic spectral data of the ligand and it's suggested structure metal complexes

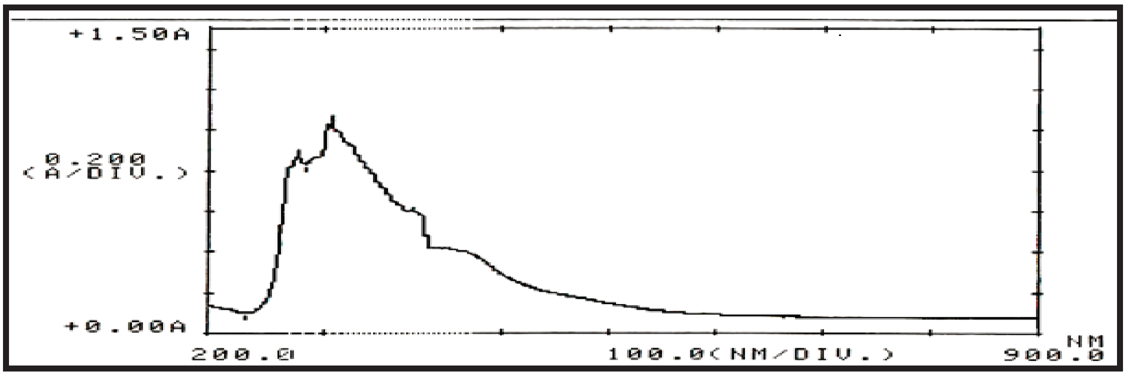
Comp.	λnm	cm^{-1}	Σ_{max} (molar^{-1}. cm^{-1})	Assignment	□^{a}S cm^{-1}. ml^{-1}	Propose structure	μeff BM
HL	280 304	35714 32895	866 1040	π—π^{*} n—π^{*}			
[C1]	290 431 625	34482 23201 16000	2200 1005 20	L.F $^{4}A_{2}g(F)\rightarrow{}^{4}T_{2}g(F)$ $^{4}A_{2}g(F)\rightarrow{}^{4}T_{2}g(F)$, ^{4}Eg	78	Octahedral	3.51
[C2]	300 390 470	33333 25641 21276	2500 1500 500	Ligand field $^{6}A_{1}g\rightarrow{}^{4}T_{2}g$ $^{6}A_{1}g\rightarrow{}^{4}E_{2}g$	18	Octahedral	4.95
[C3]	304 530	32894 18867	615 200	C.T $^{6}A_{2}g\rightarrow{}^{4}T_{2}g$	65	Octahedral	4.70
[C4]	385 603 670	25974 16583 14925	1219 88 123	C.T $^{4}T_{1}g(F)\rightarrow{}^{4}T_{2}g(p)$ $^{4}T_{1}g(F)\rightarrow{}^{4}A_{2}g(F)$ $^{4}T_{1}g(F)\rightarrow{}^{4}T1g(p)$	9	Octahedral	2.95
[C5]	288 317 408 490	34722 31545 24509 20408	1200 1099 622 50	L.F C.T $^{3}A_{2}g\rightarrow{}^{3}T_{1}g(P)$ $^{2}A_{2}g\rightarrow{}^{3}T_{1}(F)$	22	Octahedral	2.55
[C6]	299 360 375 650	33444 27777 26315 15384	1200 1099 622 52	L.F C.F $^{2}B_{2}g\rightarrow{}^{2}A_{1}g$ $^{2}B_{1}g\rightarrow{}^{2}B_{2}g$	37	Octahedral	1.94
[C7]	280 360	35714 27777	1252 550	L.F C.T	65	Octahedral	0
[C8]	288 368	34722 27173	800 890	L.F C.T	68	Octahedral	0
[C9]	288 437	34722 22883	1080 195	L.F C.T	61	Octahedral	0



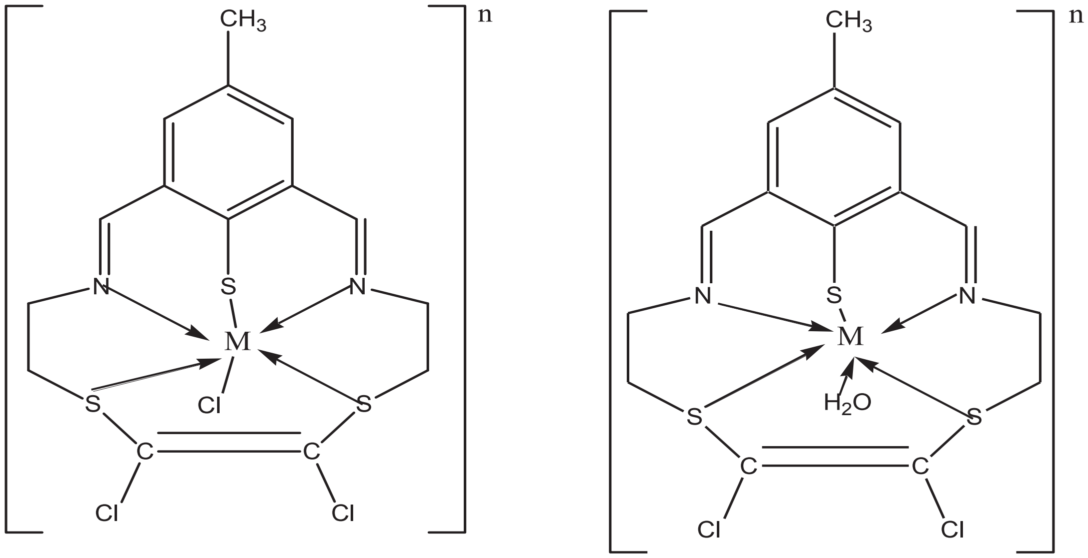
Figure(1):^{1}H NMR spectrum of HL ligand in d6-DMSO solution



Figure(2): UV-Visible spectrum of HL absolute ethanol



Figure(3): UV-Visible spectrum of Fe (III) complex in DMF solution.



M=Cr^{III}, Fe^{III}, n= +1
M=Mn^{II}, Ni^{II}, Cu^{II}, n=0

M=$Zn^{II,}$ Cd^{II}, Hg^{II}, n=+1

Figure:(4)stereo chemical structures of the prepared complexes.