Synthesis and characterization of new acyclic octadentate ligand and its complexes

F. H. A. Al-Jeboori[1], K. K. Hammud[1]* and M. J. Al-Jeboori[2]

[1]*Ministry of Science and Technology, Baghdad, Iraq*
[2]*College of Education-Ibn-Al-Haitham, Baghdad University, Baghdad, Iraq*
E-mail: kafaa_khalaf@yahoo.com

Abstract

The reaction of an equivalent of 2- mercaptoethyl ammonium chloride with an equivalent of 2,6-diformyl -4-methyl phenol produced monoamine which was reacted with half equivalent of 1,2-diamine ethane to produce ethylene-bis-6-(2-mercapto-ethyl-imine)-methyl -4- methyl phenol [H_4L]. The ligand was reacted with metal ions[Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II)] at reflux ethanol, under nitrogen at atmosphere. The ligand and derivative 2,6-diformyl-4-methylphenol and metal ion complexes were characterized by elemental microanalysis, IR, UV, (^{1}H, ^{13}C, ^{1}H-^{1}H, ^{1}H-^{13}C)NMR and mass spectroscopies and suggested structures and octahedral for the complexes [Cr, Mn, Co, and Ni] while complexes of [Fe, Zn, Cd, and Hg] suggested tetrahedral geometry and a distorted square planar geometry around copper complex.

Keywords: Schiff base; metal ion; 2-mercaptoethyl ammonium chloride; synthesis; acyclic octadentate

1. Introduction

Schiff bases (anils, imines, or azomethines: RHC=N-R1 (Cimerman et al., 2000) where R and R1 are alkyl, aryl, or heterocyclic groups which may be variously substituted) are condensation products of primary amines with carbonyl compounds where the presence of a lone pair of electrons in an sp (Patel et al., 1999) hybridized orbital of nitrogen atom is of chemical and biological importance (Patel et al., 1999).

They are excellent chelating agents (Patai, 1970) with the metal ion and this is a result of the relative easiness of preparation, synthetic flexibility, and the special property of C=N group.

Schiff bases can be applied in a variety of field such as biological (Ye et al., 2007, Nair et al., 2012; Palczewski et al., 2000) (as plant growth regulators, antimycotic, or linkage in the retina of the eye), pharmacological activities (Wadher et al., 2009) (such as antimalarial, anticancer, antitubercular, anti-inflammatory, antimicrobial, and antiviral), analytical in potentiometric sensors (Gupta et al., 2006) for specific metal ions, and industrial applications (Ashassi-Sorkhabi et al., 2004) (e, g catalysis, hydrogenation of olefins, or as an effective corrosion inhibitor which is based on their ability to spontaneously form a monolayer on the surface to be protected).

Their metal complexes have been widely studied and applied (Cozzi, 2004). There is great interest in synthesis and characterization of ligands which contain O, N, S sequence and their metal complexes so the present work was oriented towards synthesis of poly dentate ligand with its metal complexes.

2. Results and Discussion

New polydentateligand with $N_4O_2S_2$ donor atoms have been synthesized. In general the ligand contains four labile protons [H_4L] and an anionic polydentate system is formed by removing these protons.

This ligand was prepared to change the properties of the ligand from hydrophilic to lipophilic, change redox behavior of the prepared complexes, and observe the effect of cyclization on the coordination with metal ions.

The ligand was synthesized from the reaction of one equivalent of 2-mercaptoethyl ammonium chloride with one equivalent of 2,6-diformyl-4-methyl phenol. The reaction was carried out in methanol at reflux.

The reaction mixture was reacted with half equivalent of 1,2-diamineethane to produse octadentate ligand with $N_4O_2S_2$ donor atoms according to the following Scheme (1).
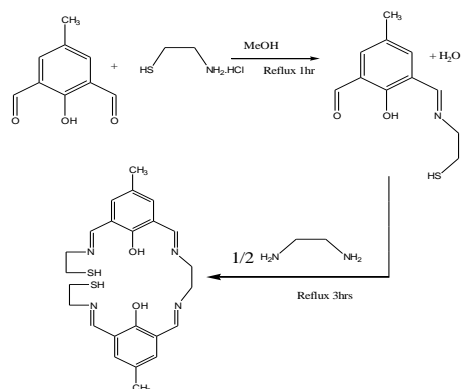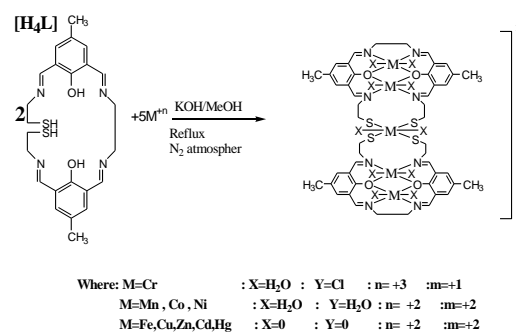
Scheme 1. The Synthesis Route of [H₄L]

The ligand ($C_{24}H_{30}N_4O_2S_2$, M.wt: 470) was obtained in a high yield (80%) as an orange crystalline, m.p (280–284ºC), soluble in water, DMSO, DMF, ethanol and methanol but not soluble in dichloromethane or chloroform. CHN analysis [found (calculated)] for this compound was done C%: 61.22 (61.24), H%: 6.42 (6.37), N%: 11.90 (11.92).

The complexes were prepared by a similar method, from the reaction of the ligand with metal chloride salt, according to general method shown in Scheme 2.

Where: M=Cr   : X=H_2O : Y=Cl   : n= +3   :m=+1
M=Mn , Co , Ni   : X=H_2O : Y=H_2O : n= +2   :m=+2
M=Fe,Cu,Zn,Cd,Hg   : X=0   : Y=0   : n= +2   :m=+2

Scheme 2. The Synthesis Route of The [H₄L]

The reaction was carried out in methanol, at reflux and under nitrogen atmosphere, in the presence of KOH as a base. The choice of base was important and no pure complexes could be isolated using another base.

The complexes were soluble in DMSO and DMF but not in water or CH_2Cl_2.

Microanalysis of the complexes along with metal and chloride analyses are in good agreement with the calculated values, Table 1.

Table 1. Elemental Analysis Results of [H₄L] and Its Metal Complexes

Empirical Formula	M.wt	Microanalysis found (Calc.) %				
		C	H	N	Metal	Cl
$C_{24}H_{30}N_4O_2S_2$	470.18	61.35 (61.25)	6.40 6.42	11.94 11.90	—— ——	—— ——
$[Cr_5(C_{24}H_{26}N_4O_2S_2)_2(H_2O)_5Cl_5]Cl_2$	1467.42	40.01 (39.56)	3.46 (3.57)	7.75 (7.69)	17.75 (17.71)	17.01 (16.93)
$[Mn_5(C_{24}H_{26}N_4O_2S_2)_2 (H_2O)_{10}] Cl_2$	1465.65	39.65 (39.15)	3.73 (3.53)	7.40 (7.61)	18.50 (18.85)	4.91 (4.84)
$[Fe_5(C_{24}H_{26}N_4O_2S_2)_2] Cl_2$	1290.2	42.01 (44.65)	4.11 (4.03)	7.88 (8.68)	19.90 (21.64)	5.665 (5.50)
$[Co_5(C_{24}H_{26}N_4O_2S_2)_2 (H_2O)_{10}] Cl_2$	1491	38.51 (38.63)	3.41 (3.48)	7.43 (7.51)	19.98 (14.77)	4.82 (4.76)
$[Ni_5(C_{24}H_{26}N_4O_2S_2)_2 (H_2O)_{10}] Cl_2$	1484.55	39.01 (38.80)	5.01 (4.84)	7.66 (7.54)	20.03 (19.77)	5.01 (4.78)
$[Cu_5(C_{24}H_{26}N_4O_2S_2)_2] Cl_2. H_2O$	1346.7	43.01 (42.77)	3.90 (4.00)	8.50 (8.31)	24.01 (23.59)	5.50 (5.27)
$[Zn_5(C_{24}H_{26}N_4O_2S_2)_2] Cl_2.H_2O$	1355.85	43.19 (43.31)	3.85 (3.41)	8.33 (8.42)	24.71 (24.57)	5.41 (5.33)
$[Cd_5(C_{24}H_{26}N_4O_2S_2)_2] Cl_2.H_2O$	1253.8	46.01 (45.94)	4.41 (4.30)	8.99 (8.93)	45.01 (44.8)	5.71 (5.66)
$[Hg_5(C_{24}H_{26}N_4O_2S_2)_2] Cl_2.H_2O$	2032.1	28.66 (28.75)	2.63 (2.59)	5.63 (5.59)	50.03 (44.42)	3.55 (3.54)

(Calc.) Calculated

The (I.R) spectrum for the starting material (cystamine) 2-mercaptoethyl ammonium chloride was shown in and 1,2-diamine ethane exhibited bands at (3335, 3320 and 1615)cm⁻¹ attributed to the ν(NH_2) symmetrical and asymmetrical stretching and (NH_2) bending respectively.

The (I.R) spectrum for [H₄L] displayed a weak absorption band at (2921) cm⁻¹ assigned to ν(C–H) confirmed by δ (CH_2) bending vibration at 1348 cm⁻¹ (William et al., 1988). The sharp double bands at (1627 and 1598) cm⁻¹ were assigned to asymmetric and symmetric ν(C=N) group (Sanmartin et al., 2000; Nakamoto, 1978), and the

same reasoning could be used for interpretation. The broad band at (3431) cm^{-1} is assigned to ν(OH), while the band at (1226)cm^{-1} was assigned to ν(C-O) (Tümer et al., 1999b; Köksal et al., 1996).

The medium band at (1037) cm^{-1} is attributed to ν(C–S) (Silversteinet al., 2005). The spectrum showed a weak band at (2586) cm^{-1} which is attributed to ν(S–H). This band was shifted by (61) cm^{-1} to higher frequency in comparison with that in cystamine at (2525)cm^{-1}. The assignment of the characteristic bands is summarized in Table 2.

Table 2. Infrared spectral data (Wave Number, ν) cm^{-1} of the ligand and starting materials

Cystamin	ν (C–S): 1100 w, ν(CH$_2$):,2900m, ν(SH): 2525$_{(w)}$,ν(NH$_2$): 3000m, δ(NH): 1530w,
1,2 diamineethylene	ν(NH$_2$): 3335$_{(s)}$ 1615
H$_4$L	ν (C=N): 1627$_{(s)}$ 1598, ν (C=C): 1512, 1461, ν (C–S): 1037$_{(m)}$,ν(CH) al., ar: 2921$_{(w)}$,2871, ν(C–O): 1226$_{(m)}$, ν(CH$_2$): 1345$_{(m)}$, ν(OH): 3431$_{(br)}$,ν(SH): 2558$_{(w)}$

S=strong; m=medium; w=weak; al.=aliphatic, ar.=aromatic

The (I.R) spectra of all prepared metal complexes showed the assignment of the characteristic bands is summarized in Table 3.

The spectrum of the ligand [H$_4$L] showed strong double bands at (1627, 1598) cm^{-1} may be assigned to asymmetric and symmetric stretching ν(C=N) (Köksal et al., 1996). In the complexes these bands were observed as double bands and were shifted to lower wave number at (1620, 1598, 1623, 1600 and 1623, 1598) cm^{-1} for the prepared (Cr), (Mn), and (Fe) complexes respectively.

These results confirm that, the nitrogen atoms of azomethine groups are coordinated to the metal ions, and a π-back bonding has occurred (Smith et al., 1989).

The (I.R) spectrum of [H$_4$L] ligand exhibited band at (1226) cm^{-1} assignable to the phenolic ν(C-O) vibration. In the complexes this vibration is shifted to higher wave number and appeared at (1228, 1228 and 1259) cm^{-1} for compounds (Cr), (Mn), and (Fe) respectively. This can be attributed to the increase of bond order of (C-O) group, upon complexization with metal ions.

This evidence indicated the coordination of the oxygen atom of the phenolic group to the metal ions (Tümer et al., 1999a). The medium band at 1037 cm^{-1} assignable to the ν(C-S) vibration in the ligand [H$_4$L], has been shifted to higher wave number and appeared at (1065, 1041 and 1039) cm^{-1} for (Cr), (Mn), and (Fe) complexes. This shifting indicated that, the sulfur atoms of the (C-S) groups are coordinated to the metal ions (Mandal et al., 1988).

The bonding of the metal ions to the ligand through the nitrogen, oxygen and sulfur atoms is further supported by the presence of new bands at

(570-440), (489-440) and (430-414) cm^{-1} ranges due to ν(M-N), V(M-O) and ν(M-S) stretching vibration (Bushweller et al., 1984).

The (I.R) spectra for (Cr) and (Mn) complexes showed bands due to ν(O-H) and (O-H) at (3421,3363) (broad) and at (3809,819) (weak) respectively, suggesting the presences of coordinated water in complexes (Nakamoto, 1978). The (I.R) spectra of the other complexes are summarized in Table 3.

The ^{1}H, ^{13}C, ^{1}H–^{1}H and^{1}H–^{13}C correlated NMR analysis were used to characterize the ligand and precursor. The spectra have been recorded in DMSO–d$_6$ solution.

In the solution, as in the solid state, it is clear that an intramolecular hydrogen bonding between the hydrogen of the phenolic group and the nitrogen atom of the imine group has occurred.
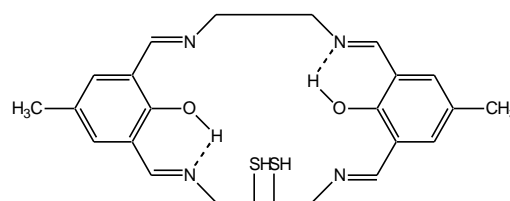
The ^{1}HNMR spectrum for [H$_4$L] in DMSO-d$_6$ showed a signal at chemical shift (δ$_H$=8.65ppm, (4H, br, N=C-H)) assignable to protons of azomethine groups (Sanmartín et al., 2000),(C$_{8,13,21,24}$). The broadness of this signal is due to occurrence of hydrogen bonding and subsequently the azomethine groups being non-equivalents.

The doublet signals at (δ$_H$=7.36 and δ$_H$=7.15ppm, 4H, d, Ar–H) are related to protons of aromatic ring(C$_{3,5,15,17}$). The appearance of these protons as a doublet is a result of mutual coupling (Atkins et al., 1996). The broad chemical shift at(δ$_H$=13.84ppm, 2H, br, O-H) can be attributed to the protons of the (O-H) phenolic group (C$_{1,19}$).

The multiplet signals are located at (δ$_H$=3.30–2.85ppm) region which is equivalent to four protons are assignable to protons of methylene (–SCH_2) groups (Köksal et al., 1996; Atkinset al., 1996) (C$_{11,10}$) (4H, m, SCH_2–, J_{H-H}=20Hz). The multiplet signal at (δ$_H$=3.85–3.41ppm) range (8H, m, NCH_2–, J_{H-H}=18Hz) which is equivalent to eight protons are assignable to protons of (–NCH_2–) groups, (C$_{9,12,22,23}$).

The resonance of the two methyl groups are equivalent and appear as a sharp singlet at (δ$_H$=2.21 ppm, 6H, S) (Huang et al., 2001). The resonance is equivalent to six protons. The above chemical shift assignments were supported by ^{1}H–^{1}H, 2D correlated NMR spectrum. All details are summarized in Table (4).

Table 3. Infrared Spectral Data (cm^{-1}) of the Ligand [H$_4$L] and its Metal Complexes

Comp.	ν (C=N)	ν (C=C)	ν(S-CH$_2$) ν(S–H)	ν(C–S)	ν(C–H)Al ν(C–H)Ar	ν(–CH$_2$)	ν(C–O)	ν(–OH)	Additional peak ν (M-N), ν (M-O), ν (M-S)
[H$_4$L]	1627$_{(s)}$ 1598	1461	1269$_{(w)}$ 2586$_{(w)}$	1037$_{(m)}$	2921$_{(w)}$ 2871	1348	1226$_{(m)}$	3431$_{(br)}$	——
CR	1620$_{(s)}$ 1598	1445	—— ——	1065$_{(m)}$	2921$_{(w)}$ 2808	1348	1228$_{(m)}$	3421$_{(br)}$	516, 468, 420
MN	1623$_{(s)}$ 1600	1440	1274 ——	1041$_{(m)}$	2923$_{(w)}$ 2858	1348	1228$_{(m)}$	3363$_{(br)}$	520, 489, 430, 414
FE	1623$_{(s)}$ 1598	1450	1259 ——	1037$_{(m)}$	2921$_{(w)}$ 2818	1350	1259$_{(m)}$	3402$_{(br)}$	575, 550, 440, 420
CO	1622$_{(s)}$	1448	1271 ——	1051$_{(m)}$	2918$_{(w)}$ 2868	1340	1232$_{(m)}$	3398$_{(br)}$	490, 440, 414
NI	1629$_{(s)}$	1450		1058$_{(m)}$	2921$_{(w)}$ ——	1342	1232$_{(m)}$	3392$_{(br)}$	528
CU	1631$_{(s)}$ 1604	1444	1278	1045$_{(m)}$	2921$_{(w)}$ 2860	1340	1232$_{(m)}$	3436$_{(br)}$	587, 513
ZN	1627$_{(s)}$	1450	1268	1041	2920$_{(w)}$ 2862	1345	1230$_{(m)}$	3440$_{(br)}$	572, 487, 440
CD	1629$_{(s)}$	1444	1270	1035$_{(m)}$	2918$_{(w)}$ 2862	1348	1224$_{(m)}$	3434$_{(br)}$	550, 460, 420
HG	1625$_{(s)}$ 1595	1448	1278	1042$_{(m)}$	2918$_{(w)}$ 2870	1344	1228$_{(m)}$	3440$_{(br)}$	570, 490, 430

CR: [Cr$_5$(L)$_2$.(H$_2$O)$_5$(Cl)$_5$]Cl$_2$, MN:[Mn$_5$(L)$_2$.(H$_2$O)$_{10}$]Cl$_2$, FE: Fe$_5$(L)$_2$]Cl$_2$, CO: [Co$_5$(L)$_2$.(H$_2$O)$_{10}$] Cl, NI: [Ni$_5$(L)$_2$.(H$_2$O)ˑ.] Cl$_2$, CU: [Cu$_5$(L)$_2$(Cl)$_2$](H$_2$O), ZN: [Zn$_5$(L)$_2$] Cl$_2$(H$_2$O), CD: [Cd$_5$(L)$_2$] (Cl)$_2$(H$_2$O), HG: [Hg$_5$(L)$_2$] (Cl)$_2$ (H$_2$O).

The ^{13}CNMR spectrum for [H$_4$L] in DMSO–d$_6$ solvent showed resonance at chemical shifts (δ_c=164.34 and δ_c=156.71ppm) assigned to carbon atoms of azomethine groups (Köksal et al., 1996) (C$_{8,13,21,24}$), indicating that the two azomethine groups are non-equivalent due to intra-hydrogen bonding.

This result is in agreement with that obtained in ^{1}HNMR. The aromatic carbon atoms are shown in the chemical shift at (δ_c=118.53ppm, Ar–C$_{2,8}$), (δ_c=128.53ppm (Ar–C$_{3,5,15,17}$), 129.23 (Ar–C$_{6,14}$). (δ_c=132.91ppm, Ar–C$_{4,16}$) and (δ_c=147.71ppm, Ar–C$_{1,19}$) respectively (Tümer et al., 2006).

The methylene carbon atoms appeared at chemical shift (δ_c=36.51ppm), (δ_c=50.34ppm),

(δ_c=58.25ppm) and (δ_c=68.29ppm) are assigned to ($C_{10,11}$-S), ($C_{9,12}$-N) and ($C_{22,23}$-N) respectively (Tümer et al., 2006).

The carbon atoms of the methyl groups ($C_{7,20}$) have been detected at (δ_C=20.12ppm). The above chemical shift assignments were supported by ^{1}H-^{13}C, 2D correlated NMR spectrum.

Table 4. ^{1}HNMR data for the ligand measured in DMSO-$d_6$br = broad, δ_S = chemical shift, S = singlet, d = doublet

Compound	Functional Group	δ_s(ppm)[b]
[H_4L]	–OH	13.84, (2H, b)
	N=C–H	8.65, 7.62 (4H, S)
	Ar–C–H	7.32, 7.15 (4H, d, $J_{H\text{-}H}$ =12 Hz)
	–NCH_2–	3.85-3.41 (8H, M, $J_{H\text{-}H}$=18Hz)
	S–CH_2	3.30-2.85 (4H, M, $J_{H\text{-}H}$=20 Hz)
	–NCH_2–CH_2–N–	3.1 (4H, S)
	–CH_3	2.21 (6H, S)

Table 5. ^{13}C NMR data for the ligand measured in DMSO-d_6

Compound	Functional Group	δ_s(ppm)
[H_4L]	H-C=N	164.34
	(Ar-C)	118.53,128.53, 129.73, 132.91, 148.73
	NCH_2	50.34
	NCH_2CH_2N	68.29
	SCH_2	36.55
	CH_3	20.12

The ^{1}H NMR spectrum for the [Hg] complex showed no signals neither (δ=13.84 ppm) nor (δ=4.11ppm), which indicated the loss of the (O-H) and (S-H) upon complexation. The doublet signal at (δ=8.63, 8.23 ppm) and multiple signal at (δ=7.22-7.00 ppm) refer to (N=C-H) and (Ar–H) protons respectively which shifted to down field compared to that in the free ligand.

The appearance of the signal of azomethine (N=C-H) as a doublet may be related to the slightly difference in the chemical environment of the two groups. This is in accordance with the result obtained from the (I.R) data. The methyl and methylene group protons have the same positions as in the free ligand.

The laser adsorption (+) mass spectrum of the ligand [H_4L] shows the parent ion peak at (M/Z)=470.651, which corresponds to [M[+]], other fragments and their relative abundance and fragmentation sequence is shown in Scheme (3).

The molar conductivity of the complexes in (DMF) indicated the (1:1) electrolyte nature (Kette, 1975) for Cr complex and the (1:2)electrolyte nature for the others.
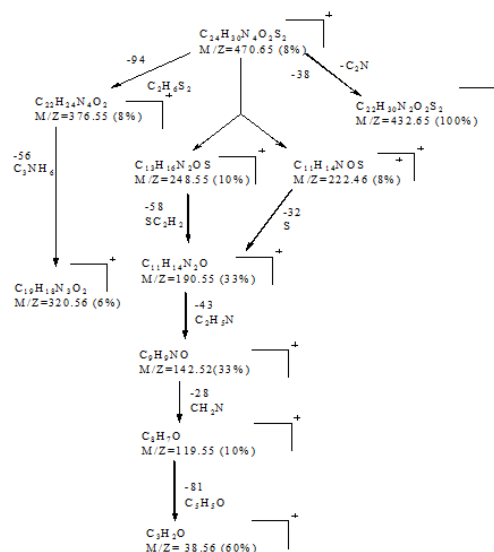
Scheme 3. The fragmentation sequences [H_4L]

Table 6. ^{1}HNMR data for the [Hg]-complex measured in DMSO-d_6.br=broad, m=multiple, d=doublet, s=sharp

Compound	Functional Group	δ_s(ppm)[b]
[Hg_5(L)_2] Cl_2.H_2O	N=C–H	8.36, 8.23 (4H, d)
	Ar–C–H	7.22–7.00 (4H, m)
	–NCH_2	3.85–3.41 (4H, m)
	S–CH_2	3.30–2.85 (4H, m)
	–CH_3	2.21 (6H, S)

The (UV) absorption data of these complexes are given in Table (8). The intense absorption peaks in the (UV) region at (284nm) (35211cm^{−1}) (ε_{max}=396molar[−1]cm^{−1}),(350 nm) (2857cm^{−1}) (ε_{max}=128 molar[−1]cm^{−1}), (270 nm) (37037cm^{−1}) (ε_{max}=1147 molar[−1]cm^{−1}), (360 nm) (27777 cm^{−1}) (ε_{max}=1470 molar[−1]cm^{−1}), (280 nm) (35714 cm^{−1}) (ε_{max}=40 molar[−1]cm^{−1}) and (340 nm) (27777cm^{−1}) (ε_{max}=4000 molar[−1]cm^{−1}) for Cr, Mn, and Fe complexes respectively were assigned to ligand field and charge transfer respectively.

Table 7. The Molar Conductivity of the Complexes

Compound	Am S.cm²·mole[−1]
[Cr_5(L)_2(H_2O)_5Cl_5]Cl_2	73
[Mn_5(L)_2 (H_2O)_{10}]Cl_2	152
[Fe_5(L)_2]Cl_2	140
[Co_5(L)_2 (H_2O)_{10}] Cl_2	145
[Ni_5(L)_2 (H_2O)_{10}] Cl_2	140
[Cu_5(L)_2(H_2O)_2]H_2O	140
[Zn_5(L)_2] Cl_2.H_2O	160
[Cd_5(L)_2] Cl_2.H_2O	165
[Hg_5(L)_2] Cl_2.H_2O	165

Other peaks in the visible region at (580 nm) (17241cm^{−1}) (ε_{max}=50 molar[−1]cm^{−1}), (420 nm) (22727cm^{−1}) (ε_{max}=80 molar[−1]cm^{−1}) and(440 nm)(17241cm^{−1}) (ε_{max}=50 molar[−1]cm^{−1}) are assigned to (d-d) transition type ($^4A_2g^{(F)} \rightarrow {}^4T_2g^{(F)}$) ($^6A_1g^{(F)} \rightarrow {}^6T_2g^{(p)}$) and (B_2 →E) for Cr, Mn, and Fe complexes respectively (Oberhausenet al., 1991).

The intense absorption peaks in (UV) region at (270nm)(37037cm^{-1}) (ε_{max}=1805 molar^{-1}cm^{-1}),(271nm) (36900cm^{-1}) (ε_{max}=2664 molar^{-1}cm^{-1}), (280 nm) (35714cm^{-1}) (ε_{max}=4500 molar^{-1}cm^{-1}) for Co, Ni, and Cu complexes respectively assigned to ligand field.

In addition the spectrum of Ni complex showed additional peak at (344 nm) (29940cm^{-1}) (ε_{max}=942 molar^{-1}cm^{-1}) assigned to charge transfer transition. In visible region Ni complex exhibited two peaks at(404nm)(24752cm^{-1}) (ε_{max}=786 molar^{-1}cm^{-1}) and (427 nm) (23419cm^{-1}) (ε_{max}=833 molar^{-1}cm^{-1}) are attributed to (d-d) transition type ($^3A_2g^{(F)} \rightarrow ^3T_1g^{(P)}$)and ($^3A_2g^{(F)} \rightarrow ^3T_1g^{(F)}$) confirm an octahedral structure around nickel (II) ion (El-Asmy et al., 1989).

While Co and Cu complexes exhibit peak in the visible region (429nm) (23310cm^{-1}) (ε_{max}=675molar^{-1}cm^{-1}) and (913 nm) (10952 cm^{-1})(ε_{max}=40 molar^{-1}cm^{-1}) are attributed to ($^4T_1g^{(F)} \rightarrow ^4T_1g^{(P)}$) and ($^2B_1g \rightarrow ^2E_2g$) transition

for Co and Cu complexes respectively, confirm an octahedral structure around cobalt(II) ion (El-Asmy et al., 1989) and square planar structure around copper(II) ion.

The (UV–Vis) spectra of Zn, Cd, and Hg complexes exhibited two intense absorption peaks at (272nm) (36764cm^{-1})(ε_{max}=2713 molar^{-1}cm^{-1}), (397 nm) (25188cm^{-1}) (ε_{max}=3039 molar^{-1}cm^{-1}), (273 nm) (36764cm^{-1}) (ε_{max}=3656 molar^{-1}cm^{-1}),(398 nm) (25125cm^{-1}) (ε_{max}=2039 molar^{-1}cm^{-1}) ,(286 nm) (27777cm^{-1}) (ε_{max}=3900 molar^{-1}cm^{-1}) and(344 nm)(29069cm^{-1}) (ε_{max}=1940 molar^{-1}cm^{-1}) for Zn, Cd, and Hg complexes respectively are assigned to ligand field and charge transfer respectively. In addition the spectrum of Hg complex showed additional peak at(427nm)(23419cm^{-1}) (ε_{max}=1159 molar^{-1}cm^{-1}) assigned to charge transfer transition, too. Since these metal ions belong to d^{10} system, these metals do not show (d-d) transition (Abras et al., 1990).

Table 8. Electronic Spectral Data of [H$_4$L] and its Metal ComplexesRecorded in DMF

Comp.	Wave length λ nm	Wave number $\bar{v}$ cm^{-1}	ε_{max} molar^{-1} cm^{-1}	Assignment	Proposed structure
[H$_4$L]	258	38759	2395	$\pi \rightarrow \pi^*$	——
	286	34965	2019	$\pi \rightarrow \pi^*$	
	336	29761	770	$n \rightarrow \pi^*$	
	402	24875	338	$n \rightarrow \pi^*$	
CR	284	35211	396	Ligand field	Octahedral
	360	23094	128	Charge transfer	
	580	17241	50	$^4A_2g^{(F)} \rightarrow ^4T_2g^{(F)}$	
MN	270	37037	1147	Ligand field	Octahedral
	360	27777	1470	Charge transfer	
	420	23255	314	$^6A_1g^{(S)} \rightarrow T_2g$	
FE	280	35714	4000	Ligand field	Tetrahedral
	340	27777	4000	Charge transfer	
	440	22727	80	$B_2 \rightarrow E$	
CO	270	37037	1805	Ligand field	Octahedral
	429	23310	675	$^4T_1g^{(F)} \rightarrow ^4T_1g^{(P)}$	
NI	271	36900	2664	Ligand field	Octahedral
	344	29940	942	Charge transfer	
	404	24752	786	$^3A_2g^{(F)} \rightarrow ^3T_1g^{(P)}$	
	427	23419	833	$^3A_2g^{(F)} \rightarrow ^3T_1g^{(F)}$	
CU	280	35714	4500	Ligand field	Square planar
	392	25510	3436	Charge transfer	
	913	10952	40	$^2B_1g \rightarrow ^2E_2g$	
ZN	272	36764	2713	Ligand field	Tetrahedral
	397	25188	1426	Charge transfer	
CD	272	36764	3656	Ligand field	Tetrahedral
	398	25125	3039	Charge transfer	
HG	286	27777	3900	Ligand field	Tetrahedral
	344	29069	1940	Charge transfer	
	427	23419	1159	Charge transfer	

CR: [Cr$_5$(L)$_2$.(H$_2$O)$_5$(Cl)$_5$]Cl$_2$, MN:[Mn$_5$(L)$_2$.(H$_2$O)$_{10}$]Cl$_2$, FE: [Fe$_5$(L)$_2$]Cl$_2$, CO: [Co$_5$(L)$_2$.(H$_2$O)$_{10}$] Cl, NI: [Ni$_5$(L)$_2$.(H$_2$O)$_{10}$] Cl$_2$, CU: [Cu$_5$(L)$_2$(Cl)$_2$](H$_2$O), ZN: [Zn$_5$(L)$_2$] Cl)$_2$(H$_2$O), CD: [Cd$_5$(L)$_2$] (Cl)$_2$(H$_2$O), HG: [Hg$_5$(L)$_2$] (Cl)$_2$ (H$_2$O)

3. Experimental

Chemical

All common laboratory chemicals and reagents were from Aldrich and Fluka and have been used without further purifications.

Measurements

An electro-thermal apparatus Stuart melting point was used to measure the melting points. Infrared spectra were done with Shimadzu FTIR Shimadzu, Japan and Ultraviolet-Visible spectra with 1601PC, Shimadzu, Japan. Conductivity measurements were recorded at CDM 83 conductivity-meter (25°C) for $(10^{-5}-10^{-3})$M solutions of the samples in DMSO or DMF.

Mass spectra for ligand and some complexes were obtained by (+) Laser adsorption technique using BRUKER DALTONICS. All isotopes distribution was compared to a computer generated distribution pattern.

The spectra were recorded at Queen Mary, London University / United Kingdom. ^{1}H-, ^{13}C-, ^{1}H - ^{1}H, and ^{1}H - ^{13}C correlated NMR spectra for the ligands and some complexes were recorded inDMSO-d_6, D_2O using a Brucker 400 MHZ , Ex 400 MHZ and a Jeol 270 MHZ instruments with tetramethylsilane (TMS) as an internal standard. The samples were recorded at Queen Mary/University of London/United Kingdom. Elemental microanalyses were performed on a (C.H.N) analyzer, from Herause (Vario EI)at Free Berlin University/ Germany.

Synthesis steps (William et al., 1988)**:**
The compound [2,6–diformyl-4–methylphenol] was synthesized by two different methods. The first method is time consuming and required multistep reactions as well as using large quantity of starting materials. Whilst the other method is considerably more straightforward, and required less time.

First method

p-cresol (108g, 100mmol.) in H_2O (200mL) was added to a solution of NaOH (50g, 125mmol.). The mixture was stirred until a clear brown solution was obtained, stirring was continued while a (37%) solution of (CH_2O) (formaldehyde) (215g, 200mmol.) in H_2O was added.

The yellow solution was allowed to stand for 48hrs., after which time a white solid had precipitated. This was filtered and washed with saturated NaCl solution (200mL). The white precipitate was dried under section. The Na salt [Na(2,6–dimethylol–4–methyl phenolate] was dissolved in 1.5 times the amount of water and neutralized with dilute acetic acid with stirring. The free alcohol was crystallized out as white crystals, recrystallized from acetone–water, filtered and dried (90%) product, melting point (128°C).

(10g, 58mmol.) of the dried product (free alcohol) was transferred to a 3–necked round–bottom flask (1000 mL), and a solution of (3g) NaOH [0.75N], in (100mL) H_2O was added. The white suspension was stirred with an over head stirrer for (20) min., and a mixture of (10g, 58

mmol.) benzene sulfonyl chloride and (10mL) benzene was added.

The white mixture was stirred by mechanical stirrer for 3 hrs to give a white precipitate 2,6–dimethylol–4–methyl benzene sulfonyl phenol (88%), m.p. (130°C). (10.7g, 35mmol.) from 2,6–dimethylol 4–methyl benzene sulfonyl phenol, was placed in a (1000mL)round bottom flask and (46.2mL) glacial acetic acid was added. The mixture was allowed to reflux and (9g, 70mmol.) of $Na_2Cr_2O_7$ was added slowly. More oxidizing agent was added when solution became blue–green in colour.

The mixture was allowed to cool, and the solid was filtered off, washed with water and dried under section to give a pale green solid (90%) from 2,6–diformyl–4–methyl benzene sulfonyl phenol, m.p. (147°C).

(10g, 33mmol.) from 2,6–diformyl–4–methyl benzene sulfonyl phenol was added slowly to (30g) of (98%) H_2SO_4 (sulfuric acid) in a (1000mL)beaker with stirring to give a very dark solution which was stirred with cooling in an (ice–bath) for 30 min. Ice was slowly added to the stirring solution, causing the dialdehyde to crystallize out as irregular brown plates.

The brown precipitate was filtered off, recrystallized from acetone–water, washed with cold water, dried in vacuum, yielding 5g, (92%), m.p. (134°C) from 2,6–diformyl–4–methyl phenol.

Second method

The dialdehyde was prepared by a completely different method as follows. To a solution of p-cresol (10.8g, 10 mmol.) in (50mL) acetic acid, hexamethylenetetramine (Erxleben and Hermann, 2000; Al-Jeboori, 2006; Al-Jeboori et al., 2013) (28.2g, 20 mmol.) and (30g, 100mmole) of para formaldehyde were added. The mixture was allowed to stir continuously until the light brown viscous solution was obtained then heated to (70-90°C.) for two hrs.

The solution was cooled to room temperature and H_2SO_4 (10mL) concentration was carefully added. The resulting solution was refluxed for 30 min, and then on treatment with distilled water (400mL) 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. More pure product was obtained by means of recrystallization from toluene, which yielded (35%) m.p. (132-134)°C.

Synthesis of the Ligand Ethylene-*bis*–6–(2-mercapto-ethyl azomethine) -2-azomethine-4–methylphenol [H₄L].
A solution of 2-mercaptoethyl ammonium chloride (0.61g, 5.4 mmol.) in (200 mL) methanol was added gradually to a solution of (2,6-diformyl-4-methyl phenol) (0.89g, 5.4mmol.)dissolved in (200mL) methanol. The reaction mixture was refluxed for one hour, and cooled to room temperature, then 1,2 ethylene diamine (0.16g, 0.18mL, 2.7 mmol.) was added gradually.

The reaction mixture was allowed to reflux for three hours under nitrogen blanket, and an orange precipitate was observed after refluxing for two hours. The reaction mixture was cooled to room temperature. The precipitate was filtered off and washed several times with

isopropanol. The crude product was recrystallized from absolute ethanol. Yield(75 %),m.p(280–284)ºC.

Synthesis of [H₄L] Complexes

(1.4mmol.) of metal chloride dissolved in methanol (10mL) was added dropwise under nitrogen atmosphere to a solution, of [H₄L] (0.26g, 0.7mmol.) dissolved in (15 mL) methanol. The reaction mixture was stirred and pH was adjusted to *Ca* 9 by adding methanolic potassium hydroxide. The reaction mixture was filtered off and allowed to reflux for two hours. The precipitate was formed, which was then filtered off, washed several times with absolute ethanol and dried.

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