

**Synthesis and Structural , spectroscopic Study of Novel  
Tetradentate Macrocyclic Ligand Type N<sub>2</sub>S<sub>2</sub> Donor Atoms  
[Bis-N-ethyl-2,2 (1,2\_ethylene disulphide)malonamide] and  
It's Complexes with VO(II),Cr(III),Co(II) ,Ni(II),  
Cu(II),Zn(II),Cd(II) and Hg(II)**

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**Abstract**

Diethylmalonate was reacted in the first step with 2- mercaptoethyl ammonium chloride to produce the precursor (PR) : Bis-N(2-mercapto ethyl) malonamide , then (PR) reacted with 1,2-dibromoethane to give 13-membered novel tetradentate macrocyclic ligand type N<sub>2</sub>S<sub>2</sub> donor atoms (H<sub>2</sub>L) : Bis-N-ethyl2,2 ( 1,2\_ethylene disulphide ) malonamide . This ligand was reacted with some metal ions in ethanol to give series of new metal complexes of molecular formula : (VO(L).H<sub>2</sub>O(Et<sub>3</sub>NH)(Cr(L)Cl<sub>2</sub>)(Co(L)).2H<sub>2</sub>O,(Ni(L)).2H<sub>2</sub>O,(Cu(L)).H<sub>2</sub>O,(Zn(L)).H<sub>2</sub>O(Cd(L)) and (Hg(L)).H<sub>2</sub>O .

All compounds have been characterized by spectroscopic methods (FT-IR, U.V-Vis , Atomic Absorption) , microanalysis of elements (C.H.N) , magnetic susceptibility , Chloride content and molar conductivity. From the above data the proposed molecular structures for VO(II) complex is square pyramid , Cr(III) complex is octahedral while Co(II) , Ni(II) , Cu(II) , Zn(II) , Cd(II) and Hg(II) were forming tetrahedral geometry.

**Introduction;**

During the past two decades, considerable attention has been given to the chemistry of the metal complexes of ligands containing N and S donor atoms such as N<sub>2</sub>S<sub>2</sub> , N<sub>3</sub>S<sub>3</sub> , this may be attributed to their stability , biological activity and potential application in many fields such as biological systems<sup>(1,2)</sup>. The N<sub>2</sub>S<sub>2</sub> and N<sub>3</sub>S<sub>3</sub> compounds are considered to be a good coordinating ligands because they involve both hard N atom and soft S atom<sup>(3,4,5)</sup> , therefore synthesis and structural characterization of such complexes have been given good attention in recent years<sup>(6,7)</sup>.

The biological evolution of N<sub>2</sub>S<sub>2</sub> and N<sub>3</sub>S<sub>3</sub> compounds are attributed to the formation of stable chelates with transition metals ions such as nickel , copper , zinc and iron<sup>(8,9)</sup> and with technetium and

rhodium for radiopharmaceuticals applications <sup>( 10, 11 )</sup> These complexes have been prepared to provide small molecule mimics of the structure and function of such enzyme <sup>( 12- 15)</sup> In this paper we report the synthesis and characterization of novel macrocyclic ligand Bis-N-ethyl-2,2(1',2'-ethylenedisulphide) malonamide derived from the reaction of new precursor Bis-N(2-mercaptoethyl) malonamide with 1,2- dibromoethane and its complexes with VO(II), Cr(III)Co(II),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II)

### Experimental

Materials , physical measurements and Analysis : Reagents were purchased from Fluka & Merck chemical Co. IR spectra were recorded as CsI disc using Fourier transform infrared spectrophotometer shimadzu 24FT-IR-8300. Electronic spectra of the all prepared compounds were measured in the region (200-1000) nm for  $10^{-3}$  M solutions in DMF at 298 °K using shimadzu - U.V-160 ultra Violet-visible spectra photometer with  $1.000 \pm 0.001$  cm matched quartz cell. Electrical molar conductivity measurements of the complexes for  $10^{-3}$  M solution of the samples in DMF were recorded at 298 °K using a PW 9527 Digital Conductivity meter (Philips). Elemental microanalysis (C,H,N) were performed by using Elemental Analyzer Perkin-Elmer-240B, while metal contents of the complexes were determined by atomic Absorption type shimadzu (A.A-670) . Magnetic susceptibility measurements were obtained at 298 °K on the solid state applying Faraday's method using Bruker BM6 instrument. Finally <sup>1</sup>H NMR. spectrum for the ligand was recorded in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> using a Bruker 400 MHz and a Jeol 270 MHz and 60 MHz instruments with tetramethylsilane (TMS) as an internal standard.

### Synthesis of Precursor Bis-N(2-mercaptoethyl) malonamide (PR):

A (100ml) round bottom flask in ice bath at (-5 °C) was charged with (0.454g,  $4 \times 10^{-3}$  mol) 2-mercapto ethyl ammonium chloride dissolved in a mixture of dichloromethane and dioxane, then (0.32g,  $2 \times 10^{-3}$  mol) of diethylmalonate was added dropwise with stirring for (3)hrs under inert atmosphere of nitrogen gas, during which time a thick yellow precipitate formed, which was cooled at room temperature , let unreacted starting materials and ethanol were removed by distillation under reduced pressure in water bath at (50 °C) for (8) hrs to give a pale yellow oily mass which becomes solid by cooling it at (4 °C) for (14) days, washed it with (10) ml diethyl ether then recrystallization from ethanol and dried to give yield (78%) (m.p.=86 °C) .

**Synthesis of ligand Bis-N-ethyl-2, 2(1-,2 ethylenedisulphide) malonamide (H2L) :**

To (0.376g,  $2 \times 10^{-3}$  mol) of 1,2-dibromoethane in (4) ml ethanol was added dropwise to a solution of (0.224 g,  $4 \times 10^{-3}$  mol) KOH in (15) ml ethanol. The reaction mixture was stirred vigorously and refluxed for (0.5) hr then cooling at room temperature. The precursor (PR) (0.444 g,  $2 \times 10^{-3}$  mol) in methanol was then added to the above solution with stirring and refluxed for (6) hrs under nitrogen blanket. The solution was then concentrated to half its volume under reduced pressure and kept overnight. Yellowish white solid mass was formed washed with ethanol and dried, yield (82%), m.p.  $104^{\circ}\text{C}$ .

**Synthesis of Ni(II) complex (C4) :**

A mixture of H2L (0.248 g,  $1 \times 10^{-3}$  mol) in methanol (15)ml and Et<sub>3</sub>N (0.204g,  $2 \times 10^{-3}$  mol) (PH of mixture =8) dropwise with stirring to (100)ml round bottom flask contains a solution of NiCl<sub>2</sub> .6H<sub>2</sub>O ( 0.238 g ,  $1 \times 10^{-3}$  mol) in (15) ml was added methanol. The reaction mixture was allowed to reflux for (4) hrs under nitrogen atmosphere, during which time the solution colour became a green, the solvent was evaporated under reduced pressure. A deep green solid was obtained, washed with dry diethyl ether (5) ml and dried under vacuum to give yield 78% of the title complex, m.p.  $200^{\circ}\text{C}$ .

**Synthesis of other complexes (C1, C2, C3, C5, C6, C7, C8) :**

A similar method to that mentioned in preparation of Ni(II) complex (C4) was used to prepare complexes (H2L) with VO(II), Cr(III), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) by using VOSO<sub>4</sub>.H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, ZnCl<sub>2</sub>.2H<sub>2</sub>O, CdCl<sub>2</sub>.2H<sub>2</sub>O and HgCl<sub>2</sub>.2H<sub>2</sub>O. Table-I stated the quantities, reactions conditions and some physical properties of the precursor (PR), ligand (H2L) and prepared complexes (C1-C8).

**Results and Discussion :**

**Precursor (PR) :**

The precursor (PR) was prepared according to general method shown in scheme-), this precursor was characterized by elemental analysis (table-2) and IR spectroscopy. The IR spectral data (table-3) of (PR) showed two bands at  $(3415)\text{ cm}^{-1}$  and  $(2600)\text{ cm}^{-1}$  referred to  $\nu(\text{N-H})$  and  $\nu(\text{S-H})$  stretching frequency respectively<sup>(16)</sup>. In addition to these bands, a band at

(1600)  $\text{cm}^{-1}$  assigned to stretching frequency for amide carbonyl group  $\nu(\text{C}=\text{O})$ . The two bands at (152)  $\text{cm}^{-1}$  and (945)  $\text{cm}^{-1}$  have been assigned to  $\nu(\text{C}-\text{N})$  and  $\nu(\text{C}-\text{S})$  stretching frequency respectively<sup>(17)</sup>.

### Ligand (HZL) :

The (HZL) pro-ligand was prepared according to the general method shown in scheme-1. It was characterized by elemental analysis (table-2), IR spectrum (fig-1), UV-Vis spectrum (fig-4) and  $^1\text{H}$ NMR spectrum (fig-5).

The assignment OF the characteristic bands for IR spectrum of ligand are summarized in table3. The IR spectral data showed a , band at (3394)  $\text{cm}^{-1}$  due to  $\nu\text{N}-\text{H}$  of the amide group the two bands at (1597)  $\text{cm}^{-1}$  and (1142)  $\text{cm}^{-1}$  can be attributed to  $\nu\text{C}=\text{O}$  and  $\nu\text{C}-\text{N}$  respectively<sup>(18)</sup>. Also the spectrum showed . disappearance of a band at (2600)  $\text{cm}^{-1}$  which could be assigned to  $\nu\text{S}-\text{H}$  , while the band at (925)  $\text{cm}^{-1}$  and weak band at (640)  $\text{cm}^{-1}$  can be attributed to  $\nu\text{C}-\text{S}$  and  $\nu\text{C}-\text{S}-\text{C}$  respectively<sup>(19)</sup> Also.

The new medium bands which were observed at (1026)  $\text{cm}^{-1}$  and (764)  $\text{cm}^{-1}$  assigned to microcycles frame work<sup>(20)</sup> The disappearance of band ( $\nu\text{S}-\text{H}$ ) and appearance of new bands ( $\nu\text{C}-\text{S}-\text{C}$  and macrocyclic frame work )due to conform the macrocyclic ligand (H2L).

The U.V-Vis spectral data (table-4) for (H2L) exhibits two high intense absorption peaks , the first at (278) nm and the second at (302) nm are assigned to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  electronic transition respectively<sup>(21)</sup>.

The  $^1\text{H}$ NMR spectrum of the ligand (fig.-5) displayed chemical shift at (2.4) ppm which is equivalent to 4H , can be attributed to the protons of two  $\text{CH}_2$  groups bonded with two N atoms. The sharp signal at  $\delta = 2.5$  ppm attributed to 2H of  $\text{CH}_2$  group which located between two  $\text{C}=\text{O}$  groups, also signal at  $\delta = 3.2$  ppm refers to 2H of two NH groups, while the signal at  $\delta = 3.4$  ppm which is due to eight protons of  $\text{S}-\text{CH}_2$  groups , appeared as expected as singlet signal<sup>(22)</sup> .

### Complexes ( C1 - C8 ) :

The reaction of (HZL) with  $\text{VO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$  or with metal chloride salt were carried out in methanol under reflux in presence of triethylamine (scheme-2) . All complexes are stable in solution (table-4) and they dissolve in DMF solvent. On the basis of elemental analysis data (table-2) , the molecular formula for prepared complexes was assigned to be :  $(\text{VO}(\text{L})).\text{H}_2\text{O}$  ,  $(\text{Et}_3\text{NH})(\text{Cr}(\text{L})\text{Cl}_2)$  ,  $(\text{Co}(\text{L})).2\text{H}_2\text{O}$  ,  $(\text{Ni}(\text{L})).2\text{H}_2\text{O}$  ,  $(\text{Cu}(\text{L})).\text{H}_2\text{O}$  ,  $(\text{Zn}(\text{L})).\text{H}_2\text{O}$  ,  $(\text{Cd}(\text{L}))$  and  $(\text{Hg}(\text{L})).\text{H}_2\text{O}$ . The suggested

molecular formula was also supported by spectral measurement as well as molar conductivity , magnetic moments and chloride content.

**Molar Conductivity :**

The molar conductivity of the prepared complexes (C1-C8) in DMF solvent in  $10^{-3}$  M at 298 °K (table-2) indicated nonelectrolytic nature for C1, C3,C4,C5,C6,C7 and C8 complexes , while indicating electrolytic nature with 1 :1 ratio for C2 complex<sup>(23)</sup> .

**Magnetic Moment :**

The measured magnetic moment ( $\mu_{\text{eff}}$ ) for the prepared complexes are shown in (table-2) . VO(II) , Cr(III) , Co(II) , Ni(II) and Cu(II) complexes exhibit magnetic moment (1.73 , 4.28 , 4.32 ,3.24 and 1.74) BM respectively which can be a normal values for high - spin complexes compared with what have been found in the literature<sup>(24)</sup>. While magnetic measurements for Zn(II) , Cd(II) and Hg(II) complexes showed the complexes to be diamagnetic .

**Chloride Content :**

The chloride content for all prepared complexes showed that the Cr(III) complex only contains chloride , this indicated the coordination of  $\text{Cl}^-$  with Cr(III) ion (table-2).

**Atomic Absorption :**

The atomic absorption measurements (table-2) for all complexes gave approximated values for its theoretical .

**IR Spectra :**

The IR spectra for all complexes gave a different spectra in comparison with that of free ligand (H2L).

1. The IR spectral data for all complexes (table-3) showed disappearance of a band at  $(3394) \text{ cm}^{-1}$  which had been attributed to  $\nu\text{N-H}$  in IR spectrum of free ligand , this indicated the protons of two NH groups were removed and anionic ligand with (-2) charge formed ( $\text{H}_2\text{L L}^{-2} + \text{H}^+$  ).Also the spectra exhibit a shift in  $\nu\text{C-N}$  to a lower frequency and appeared at range  $(1103-1128) \text{ cm}^{-1}$  in IR spectra for all complexes when it comparison with that of free ligand , this shift in the position of  $\nu\text{C-N}$  suggests the coordination of ligand through N atoms of amide group with metal ions<sup>(25)</sup>.

2. The two bands at  $(925) \text{ cm}^{-1}$  and  $(640) \text{ cm}^{-1}$  in IR spectrum of free ligand which due to  $\nu\text{C-S}$  and  $\nu\text{C-S-C}$  respectively , were shifted to

higher frequency in IR spectra of all metal complexes (table-3) , this may refer to linkage of metal ion with ligand via S atoms <sup>(26)</sup> .

3. A weak band had been observed at range (2922-2947)  $\text{cm}^{-1}$  in IR spectra for all complexes which due to OC-H aliphatic<sup>(27)</sup>.

4. A broad band was observed around ( 3268-3350 )  $\text{cm}^{-1}$  in spectra of C1,C3,C4(fig.-2),C5,C6 and (28 (fig.-3) complexes , assigned to  $\nu\text{O-H}$  and suggested the revenge of  $\text{H}_2\text{O}$  in the crystal lattice of these complexes <sup>(28)</sup> .

5. The above observations were further indicated by the appearance of new bands in IR spectra of all complexes at (512-570)  $\text{cm}^{-1}$  and at(438-460)  $\text{cm}^{-1}$  due to  $\nu\text{M-N}$  and  $\nu\text{M-S}$  respectively (29,30) while in IR spectrum of Cr(III), complex (C2) , in addition of these bands ,a new weak band was noticed at(398) $\text{cm}^{-1}$  -a which can be characterized as  $\nu\text{Cr-Cl}$ <sup>(29, 30)</sup>.

6.  $\nu\text{V=O}$  stretching mode in IR spectrum of VO(II) complex (C1) was observed at (986)  $\text{cm}^{-1}$ <sup>(31)</sup> .

7. The IR spectrum of Cr(III) complex (C2) exhibits two new bands at (2746)  $\text{cm}^{-1}$  and (2496) $\text{cm}^{-1}$  assigned to the vibration of ammonium salt  $(\text{Et})_3\text{NH}^+$ <sup>(32)</sup> .

### **Electronic Spectra :**

The electronic spectral data for all complexes are summarized in table-4 , all spectra displayed two high intense absorption peaks , the first at range (279-300) nm and the second at range (360-446) nm assigned to ligand field and charge transfer transition respectively<sup>(33)</sup> .

### **VO(II) Complex (C1) :**

The electronic spectrum of C1 complex showed a new two absorption peaks related to square pyramid geometry→ they were observed at (566) nm and (780)nm which were assigned to (d-d) electronic transition type  $^2\text{B}_2$   $^2\text{E}$  and  $^2\text{B}_2$   $^2\text{B}_1$  respectively <sup>(33 34)</sup> .

### **Cr(III) Complex (C2) :**

The electronic spectrum of C2 complex (fig.-6) exhibits a new tow-peaks at (446)nm and (548)nm which refer to (d-d) electronic transition type

$^4A_{2g}$   $^4T_{1g}$  and  $^4A_{2g}$   $^4T_{2g}$  respectively , suggesting octahedral geometry about Cr(III) <sup>(33,35)</sup>

**Co(III) Complex (C3) :**

The new absorption peak in U.V-Vis spectrum of brown Co(II) complex (fig.-7) at (674) nm can be assigned to (d-d) electronic transition type  $^4A_{2g}$   $^4T_{1g}$  this result is a good evidence for Co(II) tetrahedral geometry <sup>(33,36)</sup> .

**Ni(II) complex (C4) :**

The electronic spectrum of greenish-brown Ni(II) complex shows a new two peaks , the first With weak intensity appeared at (510) nm can be assigned to the (d-d) forbidden electronic transition  $^3T_{1g}$   $^1T_{2g}$  and the second at (680) nm can be assigned to (d-d) electronic transition type  $^3T_{1g}$   $^3T_{1g}$ (p). In fact this result is a good agreement with previous work of Ni(II) tetra hedral geometry <sup>(33)</sup> .

**Cu(II) Complex (C5) :**

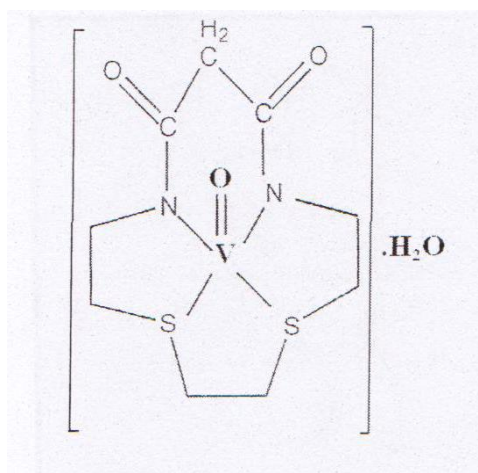
A new absorption peak at (946) nm was observed in U.V-Vis spectrum of C5 complex , which had been attributed to (d-d) electronic transition type  $^2B_{2g}$  ,  $^2A_{1g}$  apposition of this peak is a good agreement with reported for Cu(II) distorted tetrahe drat geometry <sup>(33)</sup>

**Zn(II) , Cd(II) and Hg(II) complexes (C6,C7and C8) :**

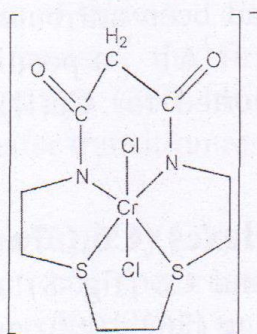
The U.V-Vis spectra of c6,C7 and C8 (fig.-8) complexes showed no absorption peak in the range (363-1000) nm , that is indicates no (d-d) electronic transition happened (d 10 - system) In the visible region , in fact this is a good evidence to Zn(II) , Cd(II) and Hg(II) tetrahedral complexes <sup>(37)</sup>

**Suggested structures :**

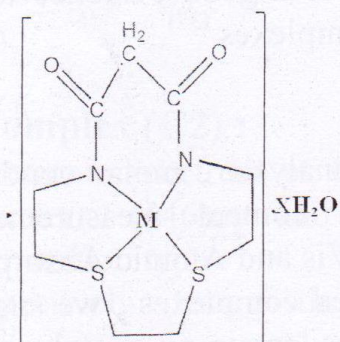
On the basis of elemental analysis , molar conductivity , magnetic moment , chloride content measurements and spectroscopic studies (IR , U.V-Vis and Atomic Absorption ) for the ligand (H<sub>2</sub>L) and all prepared complexes , we suggest that the ligand (H<sub>2</sub>L) behaves as tetradentate on complication with metal ions via N and S atoms. The following structural formula for the prepared complexes can be suggested : 1 - Square pyramid geometry for (VO(L)1.H<sub>2</sub>O



2- Octahedral geometry for  $[\text{Cr}(\text{L})\text{Cl}_2]^-$

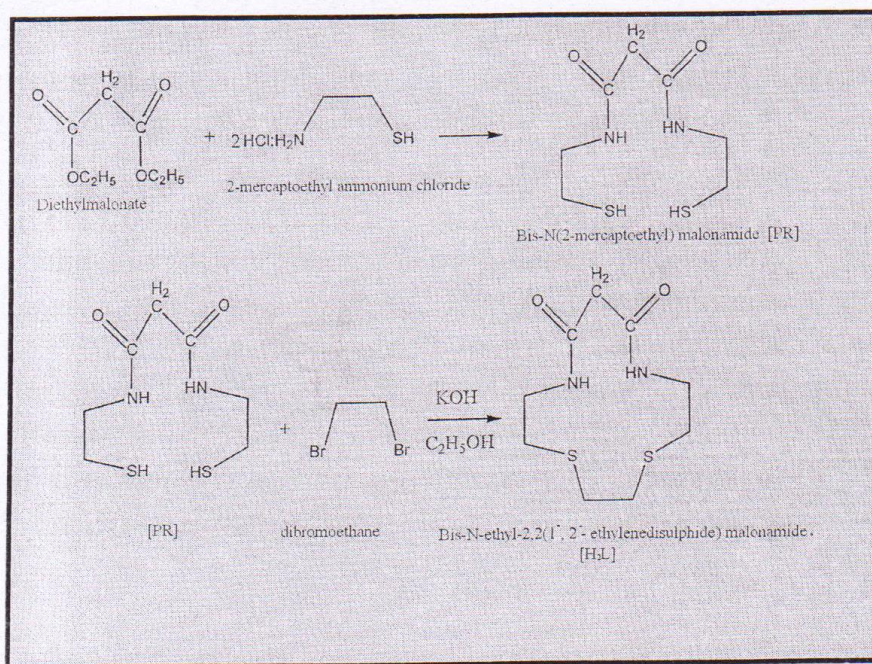


3- Tetrahedral geometry for the complexes of general formula  $[\text{M}(\text{L})]\cdot\text{XH}_2\text{O}$

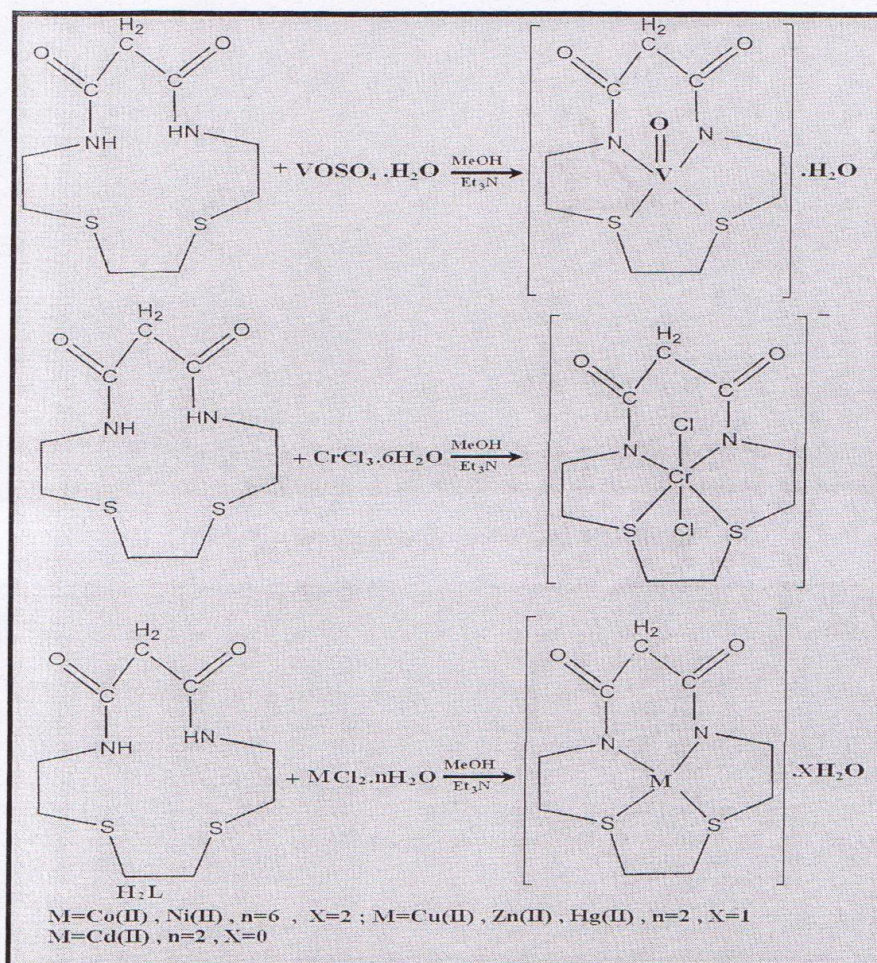


$\text{M}=\text{Co}(\text{II})$ ,  
 $\text{Hg}(\text{II})$ ,  $\text{X}=1$  ;  $\text{M}=\text{Cd}(\text{II})$ ,  $\text{X}=0$

$\text{Ni}(\text{II})$  ,  $\text{X}=2$  ;  $\text{M}=\text{Cu}(\text{II})$  ,  $\text{Zn}(\text{II})$



Scheme-1 : Synthesis method of precursor [PR] and Ligand [H<sub>2</sub>L].



Scheme-2 : Synthesis method of prepared complexes.

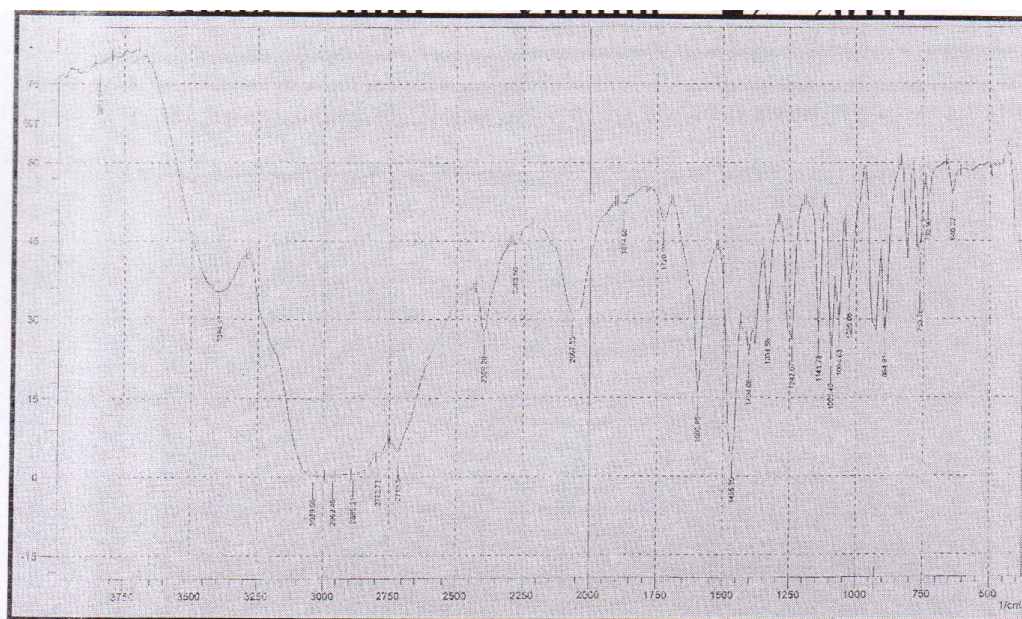


Fig.-1 : IR spectrum of ligand [H<sub>2</sub>L]

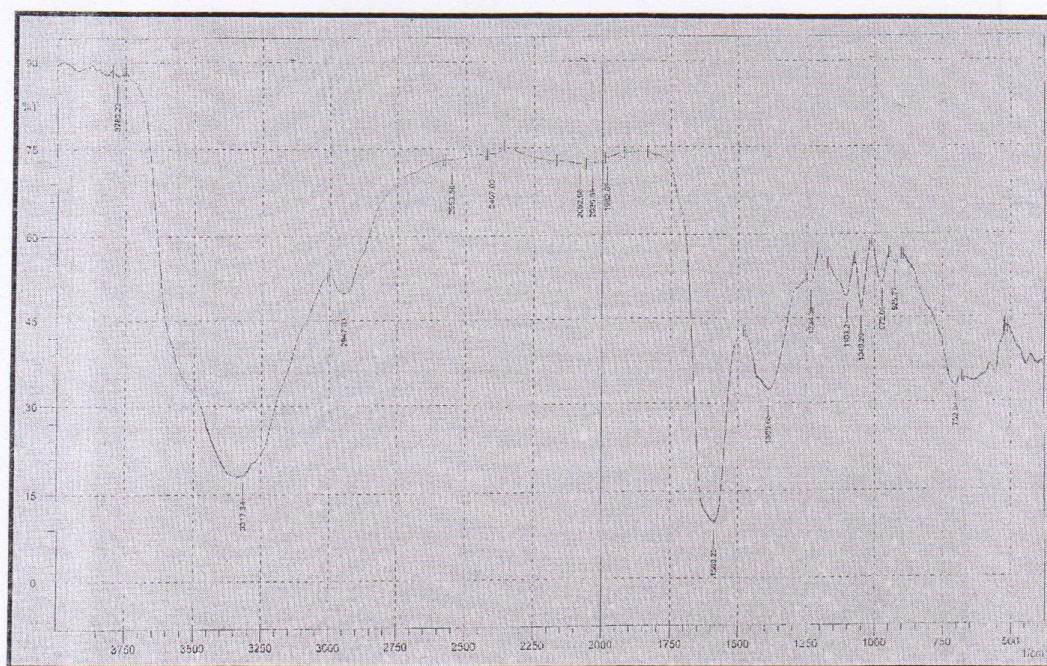


Fig.-2 : IR spectrum of Ni(II) complex (C<sub>4</sub>)

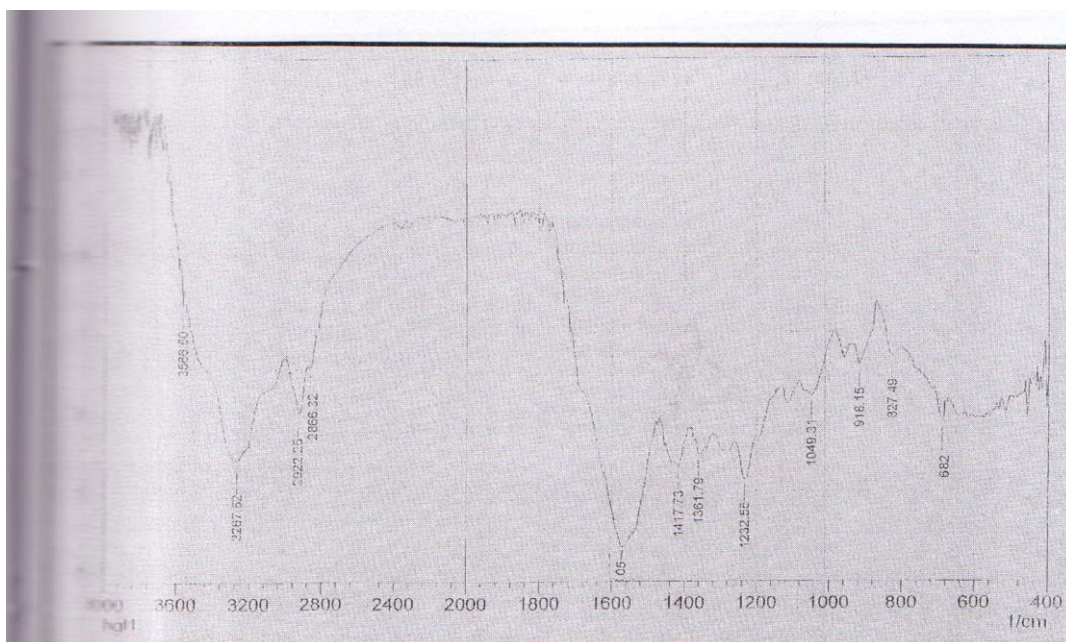


Fig.-3 : IR spectrum of Hg(II) complex (C8)

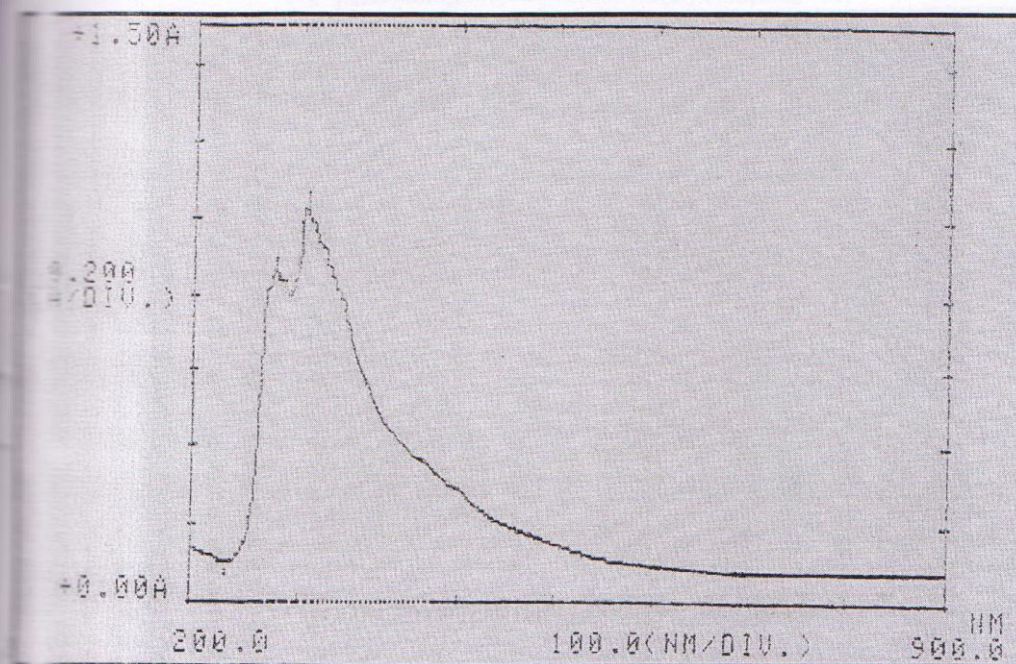


Fig.-4 : U.V-Vis – spectrum of ligand [H<sub>2</sub>L]

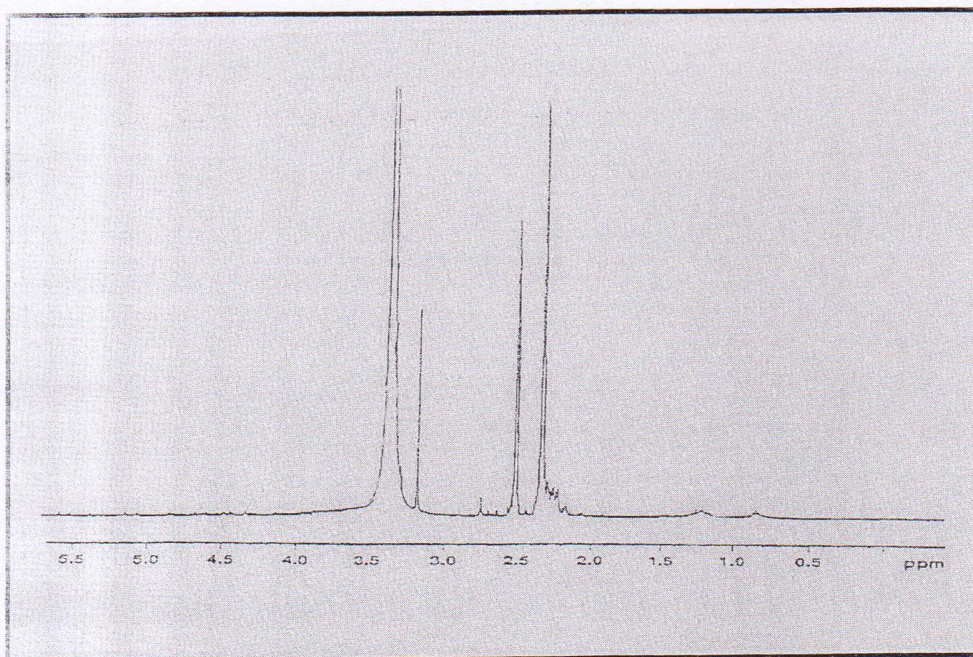


Fig.-5 :  $^1\text{H}$ NMR spectrum of ligand  $[\text{H}_2\text{L}]$

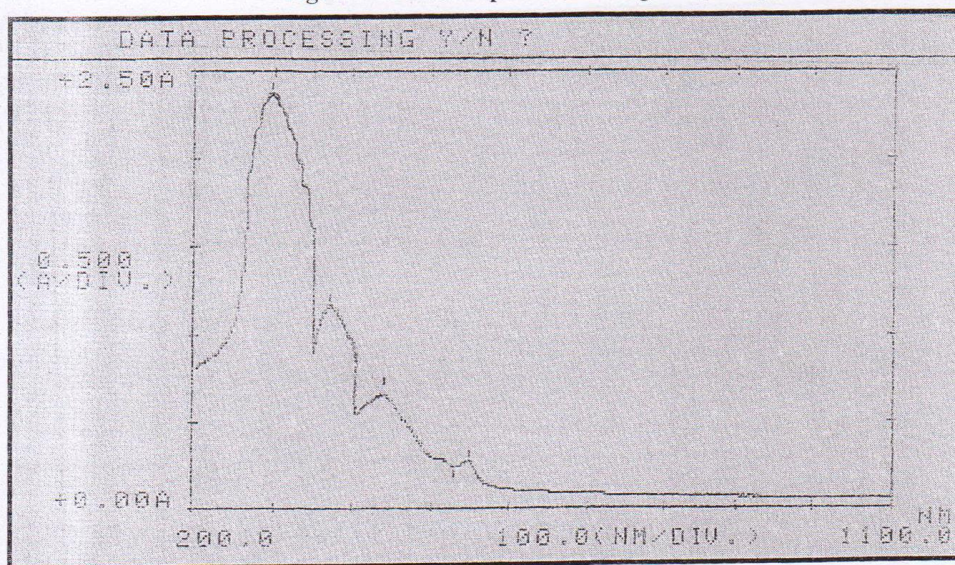


Fig.-6 : Electronic spectrum of  $\text{Cr(III)}$  complex  $(\text{C}_2)$

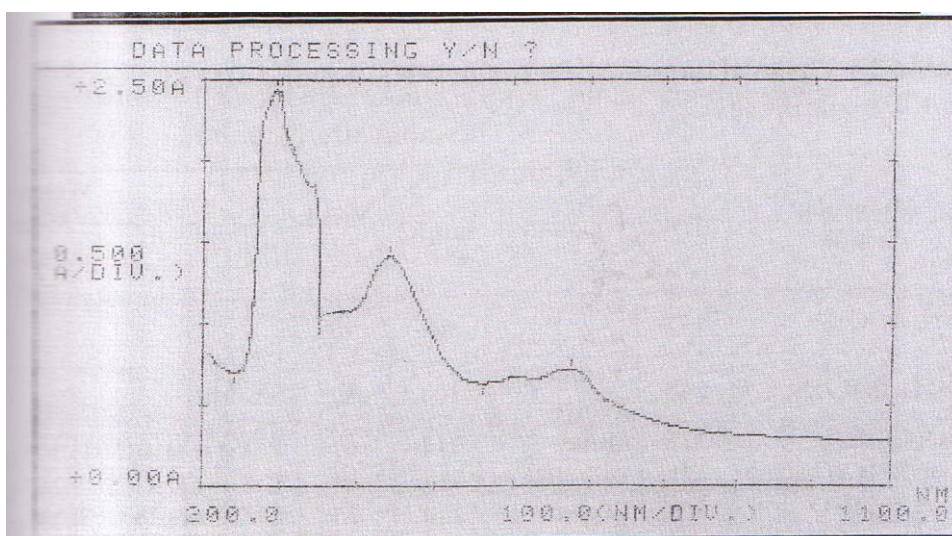


Fig.-7 : Electronic spectrum of Co(II) complex (C3)

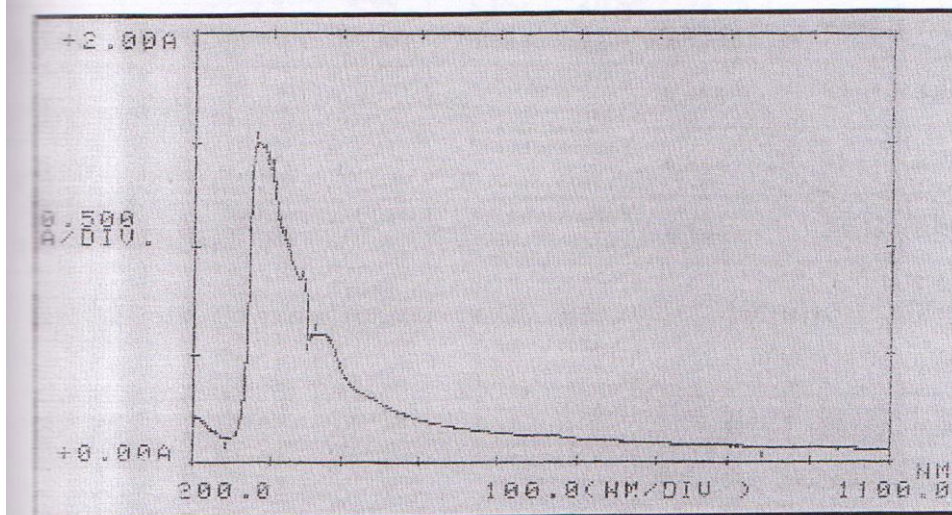


Fig.-8 : Electronic spectrum of Hg(II) complex (Cs)

**Table-1 : Physical data for precursor [PR] , Ligand [H<sub>2</sub>L] and it's complexes :**

| Symbol of compounds | Molecular formula*                                                          | M.Wt  | Colour          | m.p°C | Yield % | Metal Salt                           | Weight of Metal Salt=0.001 mol |
|---------------------|-----------------------------------------------------------------------------|-------|-----------------|-------|---------|--------------------------------------|--------------------------------|
| [PR]                | C <sub>7</sub> H <sub>14</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> | 222   | Pale yellow     | 86    | 78      | --                                   | --                             |
| [H <sub>2</sub> L]  | C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub> S <sub>2</sub> | 248   | Yellowish White | 104   | 82      | --                                   | --                             |
| C <sub>1</sub>      | [VO(L)].H <sub>2</sub> O                                                    | 325   | Olive           | 214   | 62      | VO SO <sub>4</sub> .H <sub>2</sub> O | 0.175 g                        |
| C <sub>2</sub>      | [Et <sub>3</sub> NH][Cr(L)Cl <sub>2</sub> ]                                 | 471   | Dark green      | 218   | 60      | CrCl <sub>3</sub> .6H <sub>2</sub> O | 0.267 g                        |
| C <sub>3</sub>      | [Co(L)].2H <sub>2</sub> O                                                   | 350   | Brown           | 210   | 75      | CoCl <sub>2</sub> .6H <sub>2</sub> O | 0.236 g                        |
| C <sub>4</sub>      | [Ni(L)].2H <sub>2</sub> O                                                   | 356.7 | Dark green      | 200   | 78      | NiCl <sub>2</sub> .6H <sub>2</sub> O | 0.238 g                        |
| C <sub>5</sub>      | [Cu(L)].H <sub>2</sub> O                                                    | 327.5 | Dark green      | 196   | 58      | CuCl <sub>2</sub> .2H <sub>2</sub> O | 0.171 g                        |
| C <sub>6</sub>      | [Zn(L)].H <sub>2</sub> O                                                    | 329.4 | Yellowish white | 230   | 68      | ZnCl <sub>2</sub> .2H <sub>2</sub> O | 0.173 g                        |
| C <sub>7</sub>      | [Cd(L)]                                                                     | 358.4 | Yellowish white | 236   | 70      | CdCl <sub>2</sub> .2H <sub>2</sub> O | 0.220 g                        |
| C <sub>8</sub>      | [Hg(L)].H <sub>2</sub> O                                                    | 464.6 | Yellowish white | 228   | 64      | HgCl <sub>2</sub> .2H <sub>2</sub> O | 0.308 g                        |

L = C<sub>9</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>  
(Et)<sub>3</sub>NH = (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>NH

Table-2 : Elemental analysis data , molar conductivity (M.C.) and magnetic moment ( $\mu_{\text{eff}}$ ) for prepared compounds.

| Symbol of compounds | Found % , ( Calc.) % |                |                  |                  |                  | M.C.<br>$\text{Ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ | $\mu_{\text{eff}}$ .<br>BM |
|---------------------|----------------------|----------------|------------------|------------------|------------------|-------------------------------------------------------------------|----------------------------|
|                     | C                    | H              | N                | Metal            | Cl               |                                                                   |                            |
| [PR]                | 37.62<br>(37.83)     | 5.98<br>(6.30) | 12.23<br>(12.61) | --               | --               | --                                                                | --                         |
| [H <sub>2</sub> L]  | 43.21<br>(43.54)     | 6.14<br>(6.45) | 10.91<br>(11.29) | --               | --               | --                                                                | --                         |
| C <sub>1</sub>      | 33.02<br>(33.23)     | 4.73<br>(4.92) | 8.14<br>(8.61)   | 13.26<br>(13.84) | --               | 26                                                                | 1.73                       |
| C <sub>2</sub>      | 37.93<br>(38.21)     | 5.98<br>(6.36) | 8.65<br>(8.91)   | 10.88<br>(11.04) | 14.78<br>(15.07) | 65                                                                | 4.28                       |
| C <sub>3</sub>      | 30.56<br>(30.85)     | 4.83<br>(5.14) | 7.68<br>(8.00)   | 15.92<br>(16.28) | --               | 23                                                                | 4.32                       |
| C <sub>4</sub>      | 30.02<br>(30.27)     | 4.81<br>(5.04) | 7.42<br>(7.84)   | 16.46<br>(16.73) | --               | 31                                                                | 3.24                       |
| C <sub>5</sub>      | 32.64<br>(32.97)     | 4.61<br>(4.88) | 8.21<br>(8.54)   | 19.02<br>(19.38) | --               | 29                                                                | 1.74                       |
| C <sub>6</sub>      | 32.41<br>(32.78)     | 4.46<br>(4.85) | 8.18<br>(8.50)   | 19.51<br>(19.85) | --               | 27                                                                | 0.00                       |
| C <sub>7</sub>      | 30.02<br>(30.31)     | 3.63<br>(3.90) | 7.35<br>(7.81)   | 30.96<br>(31.36) | --               | 15                                                                | 0.00                       |
| C <sub>8</sub>      | 22.86<br>(23.24)     | 3.08<br>(3.44) | 5.78<br>(6.02)   | 42.91<br>(43.17) | --               | 21                                                                | 0.00                       |

Table-3 : The most diagnostic FT-IR bands for the precursor[PR], Ligand [H2L] and it's metal complexes .

| of<br>nds | N-H      | νS-H     | νO-H    | νC=O     | νC-N     | νC-S    | νC-S-<br>C | νM-N   | νM-    |
|-----------|----------|----------|---------|----------|----------|---------|------------|--------|--------|
|           | 3415(mb) | 2600(ms) | --      | 1600(vs) | 1152(vs) | 945(vs) | --         | --     | --     |
|           | 3304(mb) | --       | --      | 1597(vs) | 1142(vs) | 925(vs) | 640(ws)    | --     | --     |
|           | --       | --       | 3314(b) | 1596(vs) | 1123(ms) | 961(vs) | 678(w)     | 556(w) | 438(w) |
|           | --       | --       | --      | 1598(vs) | 1120(ms) | 963(ws) | 672(w)     | 512(w) | 442(w) |
|           | --       | --       | 3338(b) | 1589(vs) | 1114(ws) | 960(ws) | 692(w)     | 538(w) | 452(w) |
|           | --       | --       | 3317(b) | 1589(vs) | 1103(ws) | 972(ws) | 702(w)     | 560(w) | 450(w) |
|           | --       | --       | 3350(b) | 1600(vs) | 1128(ws) | 965(ws) | 684(w)     | 546(w) | 446(w) |
|           | --       | --       | 3302(b) | 1602(vs) | 1113(ms) | 970(ws) | 692(w)     | 568(w) | 446(w) |
|           | --       | --       | --      | 1598(vs) | 1110(ms) | 968(ws) | 700(w)     | 570(w) | 448(w) |
|           | --       | --       | 3268(b) | 1583(vs) | 1120(ws) | 958(w)  | 682(ws)    | 525(w) | 460(w) |

mb = middle broad , ms = middle sharp , b = broad , ws =  
weak sharp , w = weak , vs = very sharp

Table-4 : Electronic spectral data for the ligand [H<sub>2</sub>L] and it's complexes .

| Symbol of compounds | $\lambda$<br>nm          | $\nu$ , $\text{cm}^{-1}$         | $\epsilon$<br>$\text{M}^{-1}.\text{cm}^{-1}$ | Assignment *                                                                                                                 | Suggested Structure |
|---------------------|--------------------------|----------------------------------|----------------------------------------------|------------------------------------------------------------------------------------------------------------------------------|---------------------|
| [H <sub>2</sub> L]  | 278<br>302               | 35971<br>33113                   | 856<br>1034                                  | $\pi \longrightarrow \pi^*$<br>$n \longrightarrow \pi^*$                                                                     | --                  |
| C <sub>1</sub>      | 290<br>378<br>566<br>780 | 34483<br>26455<br>17668<br>12821 | 2421<br>1018<br>604<br>261                   | L.F<br>C.T<br>${}^2\text{B}_2 \longrightarrow {}^2\text{B}_1$<br>${}^2\text{B}_2 \longrightarrow {}^2\text{E}$               | Square pyramid      |
| C <sub>2</sub>      | 300<br>373<br>446<br>548 | 33333<br>26810<br>22422<br>18248 | 2365<br>1170<br>653<br>276                   | L.F<br>C.T<br>${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{1g}$<br>${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{2g}$ | Octahedral          |
| C <sub>3</sub>      | 294<br>442<br>674        | 34014<br>22624<br>14837          | 2437<br>1412<br>717                          | L.F<br>C.T<br>${}^4\text{A}_2 \longrightarrow {}^4\text{T}_1(\text{p})$                                                      | Tetrahedral         |
| C <sub>4</sub>      | 300<br>384<br>510<br>680 | 33333<br>26042<br>19608<br>14706 | 1528<br>952<br>123<br>286                    | L.F<br>C.T<br>${}^3\text{T}_1 \longrightarrow {}^1\text{T}_2$<br>${}^3\text{T}_1 \longrightarrow {}^3\text{T}_{1(\text{p})}$ | Tetrahedral         |
| C <sub>5</sub>      | 282<br>395<br>946        | 35461<br>25316<br>10571          | 1488<br>968<br>250                           | L.F<br>C.T<br>${}^2\text{B}_2 \longrightarrow {}^2\text{A}_1$                                                                | Tetrahedral         |
| C <sub>6</sub>      | 284<br>366               | 35211<br>27322                   | 1492<br>680                                  | L.F<br>C.T                                                                                                                   | Tetrahedral         |
| C <sub>7</sub>      | 282<br>360               | 35461<br>27777                   | 1500<br>682                                  | L.F<br>C.T                                                                                                                   | Tetrahedral         |
| C <sub>8</sub>      | 279<br>362               | 35842<br>27624                   | 1493<br>562                                  | L.F<br>C.T                                                                                                                   | Tetrahedral         |

\* L.F = Ligand Field  
C.T = Charge Transfer

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تحضير ودراسة طيفية تركيبية لليكاند الحلقي رباعي السن الجديد نوع

N2S2 كذرات مانحة

[ثنائي- N - أثيل - ٢ ، ٢- ، -F - ألمجلبن ثاني سلفايد) مالونأمايد]

ومعقداته مع Hg(II) , Cd(II) , Zn(II) , Cu(II) , Ni(II) , Co(II) , Cr(III) , VO(II)

أ.م.د.ساجد محمود لطيف

قسم الكيمياء

كلية التربية / ابن الهيثم

تم في هذا البحث مفاعلة ثنائي أثيل مالونيت في الخطوة الأولى مع ٢- مركباتو اثيل كلوريد امونيوم لانتاج المشتق [ثنائي--N-- (٢- مركباتو اثيل) مالونأمايد] ثم مفاعلة هذا المشتق مع ١ ، ٢- ثنائي برمو ايثان لانتاج الليكاند الحلقي رباعي السن الجديد نوع N2S2 كذرات مانحة [ثنائي- N - أثيل- ٢ ، ٢- (١- ، ٢- اثلين ثنائي سلفايد) مالونأمايد] ثم مفاعلة الليكاند المحضر مع بعض الأيونات الفلزية في مذيب الايثانول حيث حضرت سلسلة من المعقدات الجديدة ذو الصيغ الجزئية الآتية :

. (Ni(L)).2H2O, (Co(L)).2H2O, (Et3NH)(Cr(L)C12) (VO(L)).H2O  
(Hg(L)).H2O , (Cd(L)) , (Zn(L))H2O , (Cu(L))H2O  
حيث C9H14N2O2S2 - L

شخصت جميع المركبات المحضرة بواسطة الطرائق الطيفية (تحت الحمراء . المرئية -فوق البنفسجية ، الامتصاص الذري) التحليل الكمي الدقيق للعناصر C.H.N الحساسية المغناطيسية محتوى الكلور والتوصيلية المولارية . ومن معطيات هذه التقنيات تم اقتراح الصيغ التركيبية للمعقدات وهي هيئة الهرم المربعي لمعقد VO II ثماني السطوح لمعقد CR III بينما اتخذت معقدات كل من HGII , CDII , IIZN , CUII , NI II , CO II , هيئة رباعي السطوح.