P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2013,(7), (2) :45-51 *2nd Conference For Pure Science - university of Anbar 20-22/11/2012*

Trinuclear metal complexes with hexadentate Schiff base ligand derived from diacetylbis p-phenylendiamine and salicylaldehyde

Khansa S.AL - Numa

Mosul University - College of Science

ARTICLE INFO

Received: 20 / 11 /2012
Accepted: 22 / 11 /2012
Available online: 16/2/2014
DOI: 10.37652/juaps.2013.84986

Keywords:
diacetyl;
Schiff base;
salicylaldhyde;
trinuclear;
hexadentate.

ABSTRACT

A number of trinuclear complexes with hexadentate Schiff base ligand H_2L= (a condensation product of diacetylbis p-phenylendiamine and salicylaldehyde) have been prepared . The synthesized complexes having formula [$M_2M^{-}(H_2L)_2Cl_4]Cl_2$ and $[M_2M^{-}(L)_2]Cl_2$; where M = Co(II) , Ni(II) , Cu(II) and M^{-} = Zn(II) , Cd(II) , Hg(II) . H_2L and L the neutral and dibasic forms of Schiff base . The complexes were prepared by the reaction of metal chloride with the ligand in both neutral and basic media . The ligand and its complexes were studies by means of chemical physical and spectral methods. These studies were revealed that the Schiff base act as neutral hexadentate and dibasic hexadentate ligand coordinated through the azomethine nitrogen and phenolic oxygen atoms in neutral and basic media .These studies suggested an octahedral geometry or square planar for two side metal ions in neutral and basic media respectively; The central metal atom is tetra – coordination in all complexes.

Introduction:

During the last few decades , there has been considerable interest in the chemistry of Schiff base compounds[1]. Schiff bases , containing different donor atoms , also find use in analytical chemistry for metal coordination [2,3]. Especially derivatives of salicylaldehyde and diamine have been of great interest [4,5].They act as multidentate ligands and provide suitable coordination mode for transition metal ions so that obtained complexes have great potential in catalysis and material chemistry[5,6]. our interest in this kind of ligand derives from the know ability of such ligands containing multipotencial donor atoms to synthesize and stabilize homo and hetero – multinuclear complexes[6 –8]. Multinuclear complexes themselves have attracted extensive interests due to their significant in catalysis,[9] various biological systems [10], polymers and dyes[11]

The present work includes the preparation of trinuclear complexes of Zn(II), Cd(II), Hg(II) as central atoms while Co(II), Ni(II), Cu(II) as side atoms with hexadentate (N_4O_2) Schiff base ligand H_2L which was prepared by condensation of diacetylbic p-phenylendiamine. The structure of Schiff base ligand is shown in Fig.1.

* Corresponding author at: Mosul University - College of Science, Iraq.E-mail address:

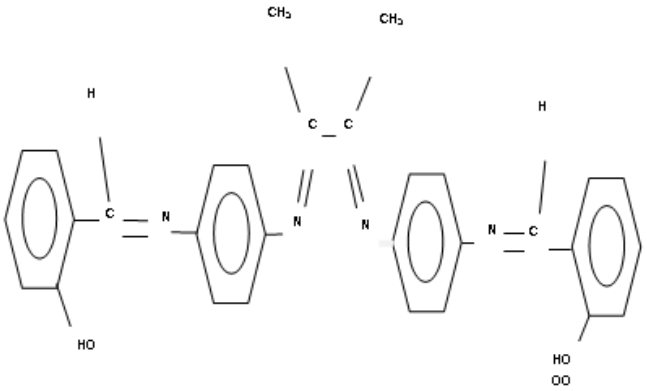


Fig. 1 : structure of Schiff base H_2L

Experimental :

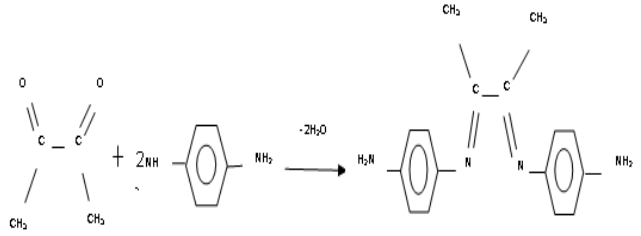
All chemicals used were of high purity (BDH or Fluke), Melting point were determined using Buchi 510 melting point apparatus . Infrared spectra were recorded using Tensor 27 Co. Bru Keo (FT,IR) spectrophotometer 400–4000cm-1 as KBr disc. The electronic spectra were recorded on Schimadzu UV. Visible spectrophotometer UV-160 for 10-3M solution of complexes in DMSO at 25C0. conductivity measurements were carriod out on 10-3M solution of the complexes in DMSO using (PMC3 (Jenway) conductivity model) at room temperature. Magnetic measurements were carried out on the solids by the Faradays method using Bruker BM6 instrument. The metal content of

complexes were determined spectrophotometric ally using Shimadzu AA670 atomic absorption spectrophotometer.

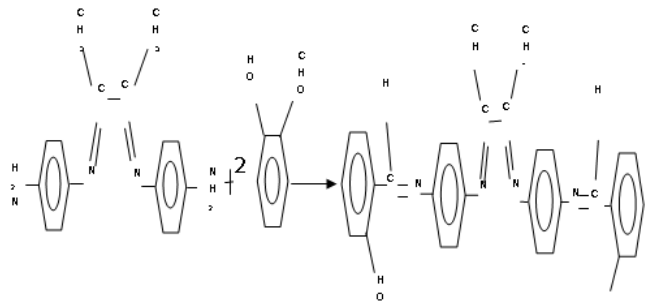
Preparation of compounds :

Preparation of the ligand [12] . H_2L = $C_{30}H_{26}N_4O_2$

A diacetyl (0.86g,0.01 mole) solution in 20 ml of ethanol was added to p- phenylendiamine (2.46 g, 0.02 mole) and stirred under reflux for 2h. The formed pale brown solid diacetylbis p-phenylendiamine was filtered off, washed with water (2x 2ml) and ether (2 ml) then dried in air. Asolution of diacetylbis p-phenylendiamine (2.66g, 0.01 mole) in 30 ml of ethanol was added to salicylaldehyde (2.44g . 0.02 mole) solution in 20ml of ethanol. The mixture was stirred under reflux for 2h. to ensure completion of the reaction. The orange precipitated ligand H_2L was filtered, washed with cold ethanol (2x3ml) and ether (3ml) then dried in air, as shown in the following equations.



Step 1:
(diacetylbisp p-phenylendiamine)



Step 2:

Fig 2 : Synthesis scheme for the preparation of the ligand (H2L)

Preparation of the complexes :

Preparation of [M_2 M^- $(H_2L)_2$ Cl_4]Cl_2 and [M_2 M^- $(L)_2$]Cl_2

Tow procedures were adopted for preparation of the complexes . In the first one ethanolic solution of the lignd (0.097g , 0.002 mole) were mixed with Zn Cl_2 .(0.12g 0.001 mole); $CdCl_2$. H_2O (0.22g) or $HgCl_2$.(0.27 g) and $CoCl_2.6H_2O$ (0.46g , 0.002 mole) ; $NiCl_2.6H_2O$ (0.46g) or $CuCl_2$.$2H_2O$ (0.26 g) . The mixture was then refluxed for 2h . with continuous string , the solid products were filtered off , washed with ethanol (20 ml) and ether (5ml) then dried . In the second procedure (0.1 N) potassium hydroxide solution was added to the reaction mixture of the metal salt and the ligand until PH 8.5 – 9 then following the above procedure , (except for washing the products with diluted ethanol)

Results and Discussion :

Several complexes of Zn(II) , Cd(II) , Hg(II) as central atoms and Co(II) , Ni(II) , Cu(II) as side atoms with Schiff base ligand were prepared and characterized .The molar conductance values of 10^{-3}M solutions of the metal complexes in DMSO are in the range (68.2 – 98.6) ohm^{-1} cm^2 mol^{-1} (Table – 1 -) indicating electrolytic nature (1:2) of these complexes[13] and divided them in to two types Type – I represent those formed in neutral medium and Type – II are those formed in basic solution , as shown in the following equations :

$2H_2L + 2MCl_2 . XH_2O + M^- Cl_2 . y H_2O \rightarrow [M_2M^- (H_2L)_2 Cl_4]Cl_2 + mH_2O$ ---- Type – I –

$2L+2MCl_2.XH_2O+M^- Cl_2.YH_2O + 4KOH \rightarrow [M_2M^- (L)_2]Cl_2+4KCl + mH_2O$ ---- Type – II –

M = Co(II) , Ni(II) , Cu(II) M^- = Zn(II) , Cd(II) , Hg(II)

X , Y = 6 – 2 m = 0 – 6

The complexes are quite stable in dry air and are very slowly affected by moisture . They are fair stable to heat and have been found to melt or decompose between 116-192 ^{0}C . They are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) . The most important I.R assignment of ligand as well as its complexes bonding sites (Table-2-) have been determined by careful comparison of the spectra of ligand and the complexes .

The infrared spectra of type – I – complexes [M_2M^- $(H_2L)_2$ Cl_4] Cl_2 show negative shift for ν(OH) bands by about 120 – 150 Cm^{-1}. This reveling the coordination of phenolic hydroxyl group without deprotonation [14] . For type – II – complexes [M_2M^- $(L)_2$] Cl_2 , the ν(OH) bands were absent . The disappearance of these bands was attributed to coordination of the ligand through deprotonation of phenolic hydroxyl group resulted in basic solution [15] (fig . 3) and (fig . 4) .

On the other hand band appeared at 1636 Cm^{-1} due to azomethine ν(C=N) stretching in free ligand is

shifted to lower frequencies by 20– 30 cm^{-1} in both types of complexes [16,17] phenolic ν (C - O) stretching vibration band is observed at 1279 Cm^{-1} in the free ligand . In all complexes this band appears at higher frequency by 12– 47 Cm^{-1} , confirming the involvement of the phenolic group in complexes [3,4] .In both types of complexes new bands at 500-550 and 430-475 Cm^{-1} can be attributed to ν (M-N) and ν (M – O) respectively [2 , 4 , 17] .

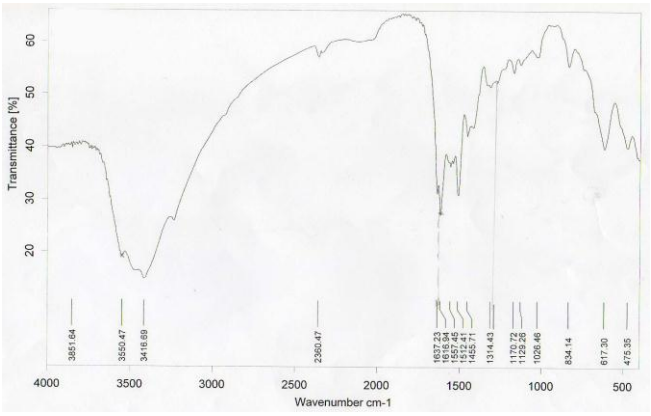
For type – I – complexes room temperature magnetic moment of Co(II) complexes (1,4,7) , are 4.80 – 4.87 B.M .The electronic spectrum shows bands at 10500 – 11100 , 14206 – 15243 and 18656 – 19300 Cm^{-1} . Thus the spectra resemble those of complexes possessing octahedral geometry[18, 19] . Assuming effective symmetry of various bands can be assigned to $^4T_{1g}$ (F) → $^4T_{4g}$ (F) (ν_1) , $^4T_{1g}$ (F) → $^4A_{2g}$ (F) (ν_2) and $^4T_{1g}$(F) → $^4T_{1g}$ (P) (ν_3) transitions respectively (fig .5) . The magnetic moment of Ni(II) complexes (2 ,5, 8) at room temperature are 2.85 – 3.11 B.M The electronic spectrum of Ni (II) complexes show three spin-allowed transition at 10000 – 10893 , 14205 – 15300 and 23750 – 29000 Cm^{-1} which are assignable to $^3A_2g(F) \rightarrow {}^3T_2g(F)$ (ν_1) , $^3A_2g(F) \rightarrow {}^3T_1g(F)$ (ν_2) and $^3A_2g(F) \rightarrow {}^3T_1g(p)$ (ν_3) respectively . Examination of these bands indicate that the complexes have octahedral geometry[19,20] . The magnetic moment of Cu(II) complexes (3,6,9) at room temperature are 1.62 – 2.15 B.M , Corresponding to one unpaired electron . The electronic spectrum show broad bands at 16000 – 17100 Cm^{-1} which were assigned to $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2Eg$ respectively . Examination of these bands indicates that the complexes have octahedral geometry [19] .

For type – II- complexes the values of magnetic moment of Co(II) complexes (10 ,13 , 16) are 2.30 – 2.59 B.M [21] . The electronic spectra of these complexes shows absorption bands at 15650 – 16790 cm^{-1} attributed to the $^2A1g \rightarrow {}^2Eg$ transition which is compatible with these complexes having a low spin square – planar structure [22] .

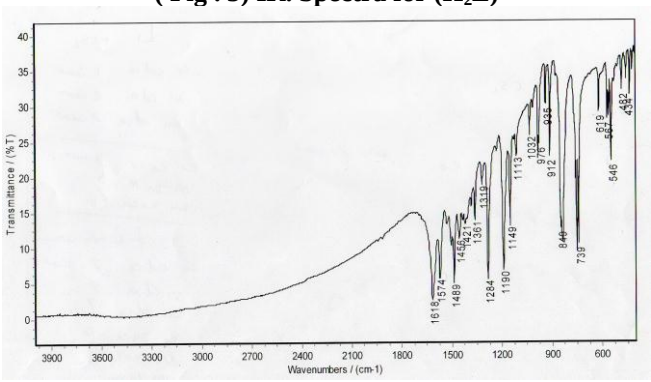
The Ni(II) complexes (11, 14 , 17) show a diamagnetic moment [23] and the electronic spectra of these complexes show bands at 15386 – 16000 cm^{-1} and 24600 – 26550 cm^{-1} which are assignable to $^1A_1g \rightarrow {}^1A_2g$ and $^1A_1g \rightarrow {}^1B_1g$ which is consistent with square planar geometry for Ni (II) complexes [24].

The Cu(II) complexes (12,15,18) show a magnetic moment 2.13 – 2.22 B.M and the electronic spectrum showed abroad band at 15612 – 17301 cm^{-1} which is assigned to combination of transition $^2B_1g \rightarrow {}^2A_1g$ and $^2B_1g \rightarrow {}^2Eg$ transition which is consistent with square planer geometry around Cu(II) complexes [25] (fig . 6) .

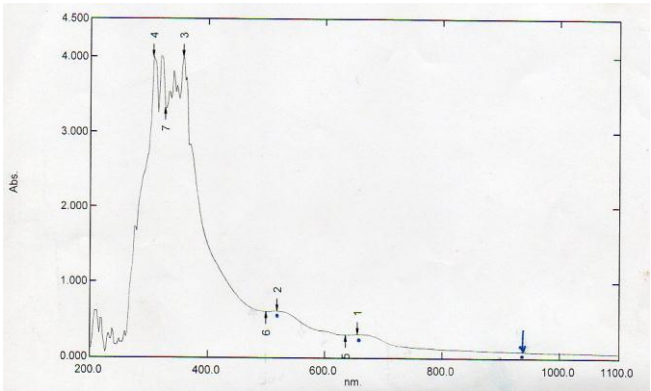
According to the above measurements ,we suggest the following structures of complexes as in (Fig . 7).



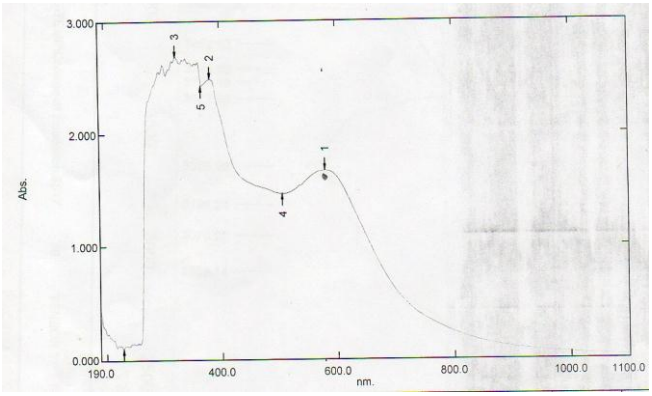
(Fig . 3) IR. Spectra for (H_2L)



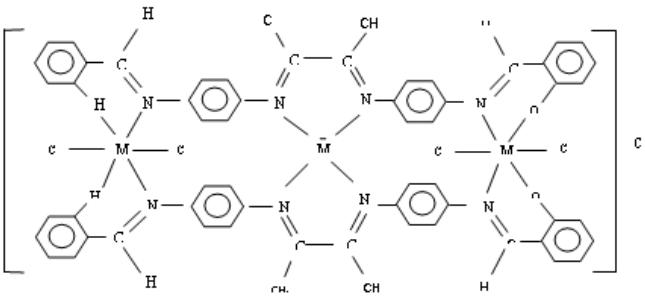
(Fig . 4) IR. Spectra for complex(15)



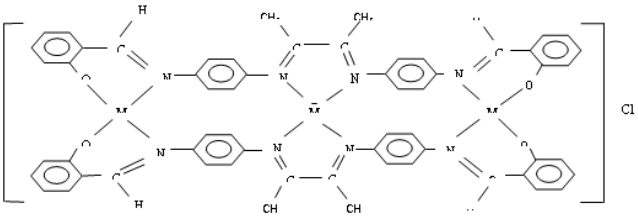
(Fig .5) UV. Spectra for complex (7)



(Fig . 6) UV. Spectra for complex (18)



(Type – I -)



(Type – II -)

Fig . 7 proposed structures for the prepared complexes

References :

1- M.T. , M.G. , B.Z., and B.N. , (2006) . Synthesis and crystal structure of Schiff based on AMTTO. Naturforsch B61 , pp 1421 – 1428

2- M.S., S.M.S. , and K.P., (2004) . Structure and conformation of Ni complex : (2- hydroxo – 3 – piperidine 1- yl – methyl – N – N – (bis – 5 – bromobenzyl – proplenedimine) Ni(II) perchlorate). Cryst . Res . Techonl , Vol. 39 , pp . 185 – 189 .

3- B.L. , S.H.M. , K.N.Sh. (2011) . Synthesis , spectal characterization and vitro microbiological evaluation of novel glyoxal , biacetyl and benzyl bis – hydrazone macrocyclic Schiff bases and the . Co(II) , Ni(II) and Cu(II) complexes . polyhedron , vol. 30 , pp. 1507 – 15011

4- O.AL- O. (2012) . Synthesis , characterization and theoretical treatment of sandwich Schiff bases complexes derived from salicylaldehyde with some transition metals and study of its biological activity . Inter . J . of chem.. Res. Vol. 2 , No. 3 pp. 1-5 .

5- M.J . and J.A. Kh. (2010). Antitumour activities of some Schiff base derived from benzoin , salicylaldehyde , amino phenol and 2 , 4 dinitro phenyl hydrazine Tha. J . Pharm. Sci Vol. 34 , pp. 20-31 .

6- R.A. , B.S. and G.V. (2008) . Variation in coordinative property of two different N2O2 donor Schiff base ligands with Ni(II) and Co(II) ions characterization.Struct. Chem. , Vol. 3 , pp.459

7- K.B. , F. D. and J.T. (2004) . New poly Fe (II) complexes of N4O dinucleating Schiff bases and pseudohalides : syntheses , structures and magnetic properties . Inorg. Chem. Vol. 43 , no. 4 , pp . 1574 – 1586 .

8- S . Z . and C. N. K. (2011) . Studies on some trinuclear Schiff base complexes Inter. J. Chem. Tech. Res. Vol. 3 , no. 4 , pp. 1962 – 1968 .

9- S. Z. and X. M. C. (2004) . Recent advances in luminescent monomeric , multinuclear and polymeric Zn(II) and Cd(II) coordination complexes . Aust. J. Chem. , Vol. 57, pp. 703-712.

10- M. T. , H. K. and M. D. (1999) Antimicrobal study of mononuclear and binuclear mixed ligand Cu(II) complexes derived from 1 , 10 – phenathroline. Trans. Met. Chem. , Vol. 24 , pp. 13 – 17

11- R. S. G. and K. E. G. (1993) . study of poly – Schiff bases rubber. Protective agent in natural rubber. Int. J. Polym. Mater. , Vol. 23 , pp. 17 – 26 .

12- N. S. and A. N. S. (2011) . Physico – Chemical and biological studies of Cu(II) , Co(II) and Ni(II) complexes of an N4 coordinating ligand derived from diacetyl bis – ethylenediamine and benzoic acid . J. Serb. Chem. Soc. , Vol. 67 , pp. 1-11 .

13- W.J. (1971). The use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord. Chem. Rev. , Vol. 7 , pp 81 – 122 .

14- M. S. , T. S. , S. M. , (2012) . some theoretical study on the interaction between of a salen Schiff – base ligand with Zn(II) , Cd(II) , Hg(II) ions. J. Chem. And phar. Res. , Vol. 4 , no. 1 , pp. 27 – 32 .

15- W.H.H. and A.E.G. (2012) . Synthesis , charact erization and antibacterial activites of new pd(II) , pt(IV) complexes of som unsymmetrical

tetradentate Schiff basses . Amer. Chem. Sci. j. , Vol. 2 , no. 3 , pp. 86 – 99 .

16- S.S. and K. D. (2005). Synthesis and spectroscopic characterization of some transition metal complexes of new hexadentate N2S2O2 Schiff base ligand spectro chimica Acta. Part A62 , pp. 383 – 393 .

17- G.C.P. , and D. A. Th. (1972) N-aryl salicyladimine complexes : IR. And PMR. Spectra of the ligand and vibrational frequencies of their metal (II) chelates. J. Iorg. Nucl. Chem. , Vol. 34 , pp. 3357 - 3367

18- S.Ch. , M.T. , K. Sh. (2009) Mn(II) , Co(II) Ni(II) and Cu(II) complexes of tetraazamacro cyclic ligand : Synthesis , characterization and biological Screening . J. Iran. Chem. Soc. , Vol. 2 , no. 3 , pp. 310 – 316 .

19- F. A. C. , G. W. , C. A. M. , and M. B. (1999) " Advanced inorganic chemistry " 6thed. , John – Wiley and Sons , New York , pp. 810 – 842 .

20- P. , R. K. A. (2008) . Ni(II) complexes of hydrazone of isoniazide and their magneto – spectral – electrochemical , thermal and antimicrobial invistigations. Res. Lett. Inorg. Chem. , ID 35091 , 1 - 4 .

21- G. w. (1987) " Comprehensive Coordination Chemistry " , Vol. 2 , Pregamon press , London , pp. 316 – 318 .

22- P. P. S. , U. P. Sh. , R.M. , and R. t. (1975) . Synthesis and structural studies of some Co(II) Cd(II) complexes with Lewis bases. J. Inorg. Nucl. Chem. , Vol. 37 , pp. 679 – 688 .

23- E. A. A. , K. S. AL – N. and O. M. AL – R. , (2010) . Synthesis and Characterization of dinuclear metal complexes stabilized by tetradentate Schiff base ligands . Amer. J.Appl. Sci. , Vol. 7 , no. 5 , 628 – 633 .

24- N. S. , N. K. S. and C. K. (1989) . Synthetic and spectroscopic heterobimetallic complexes containing diamagnetic and paramagnetic metal ions . Bull. Soc. Jap. , Vol. 62 , pp. 3328 – 3333 .

25- N. K. , F. K. , and S. K. (2007) Mono – Di – and Trinuclear Cu(II) complexes of a Schiff base ligand , 2- {(E – 6 – (1 E) – 2 – hydroxphenyl) methylen amino pyridine – 2 – yl imino imino methyl } phenol. Tur. K. J. Chem. , Vol. 3 , pp. 271 – 277.

Table 1: physical properties and metal content of the metal complexes Note; M% =Co%, Ni% andCu%

NO.	Complexes	Color	m.p (^{0}C)	Cond.Λ ohm^{-1}cm^2.mol^{-1}	Meff B.M	M%Calc. (found)
1	[Co_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Greenish yellow	160	72.5	4.80	8.76 (9.26)
2	[Ni_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Brown	178	75.0	2.85	8.74 (9.11)
3	[Cu_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Dark green	192	69.8	2.15	9.38 (9.98)
4	[Co_2 Cd $(H_2L)_2$ Cl_4] Cl_2	Greenish yellow	150	77.2	4.87	8.46 (9.02)
5	[Ni_2 Cd $(H_2L)_2$ Cl_4] Cl_2	Pale brown	181	80.3	3.11	8.44 (7.74)
6	[Cu_2 Cd $(H_2L)_2$ Cl_4] Cl_2	Orange	169	71.6	2.00	9.07 (8.62)
7	[Co_2 Hg $(H_2L)_2$ Cl_4] Cl_2	Brown	172	72.3	4.81	7.96 (8.11)
8	[Ni_2 Hg $(H_2L)_2$ Cl_4] Cl_2	Dark brown	162	76.4	3.00	7.93 (8.50)
9	[Cu_2 Hg $(H_2L)_2$ Cl_4] Cl_2	Brown	192	76.9	1.62	8.53 (8.00)
10	[Co_2 Zn (L)$_2$] Cl_2	Yellow	175	98.6	2.30	9.82 (9.20)
11	[Ni_2 Zn (L)$_2$] Cl_2	Dark brown	142	77.2	Dia	9.79 (10.29)
12	[Cu_2 Zn (L)$_2$] Cl_2	Brown	177	77.2	2.13	10.51 (10.00)
13	[Co_2 Cd (L)$_2$] Cl_2	Pale brown	140	68.2	2.59	9.45 (9.81)
14	[Ni_2 Cd (L)$_2$] Cl_2	Pale green	126	72.8	Dia	9.42 (9.01)

15	[Cu_2 Cd (L)$_2$] Cl_2	Green	178	72.5	2.22	10.12 (10.46)
16	[Co_2 Hg (L)$_2$] Cl_2	Greenish yellow	169	70.8	2.39	8.83 (9.11)
17	[Ni_2 Hg (L)$_2$] Cl_2	Brown	116	76.9	Dia	8.80 (8.18)
18	[Cu_2 Hg (L)$_2$] Cl_2	Dark brown	146	71.6	2.13	9.45 (8.99)

Table2: I.R. spectra (cm-1) and electronic spectra (Cm-1) of the ligand and their complexes s=stong; m =medium; w=weak

Comp.	H_2L	1	2	3	4	5
ν (C=N)	1637 s	1612 s	1610 s	1617 s	1615 m	1609 s
ν (OH)	3550 m	3410 m	3430 m	3415 m	3419 m	3428 m
ν (C-O)	1279 w	1326 w	1300 w	1298 m	1295 m	1318 m
ν (M-O)	-	500 s	500 s	500 s	515 m	510 m
ν (M-N)	-	433 s	470 s	471 s	430 m	432 s
Electronic spectra (Cm^{-1})		10500 , 14947 , 18656	10000 , 15300 , 23750	1600	11100 , 16100 , 19300	10893 , 14205 , 24752

6	7	8	9	10	11	12	13	14	15	16	17	18
1612	1615 m	1607 s	1615 m	1610 s	1611 s	1616 s	1612 m	1609 m	1618 s	1610 m	1608 s	
3400 w	3410 m	3402 m	3426 w									
1320 m	1315 m	1300 m	1291 m	1311 m	1298 w	1301 m	1322 m	1310 s	1319 w	1324 w	1320 m	
520 m	503 s	518 s	514 s	520 s	532 s	512 s	510 m	548 m	546 m	550 m	516 m	
466 s	450 m	472 m	475 s	460 s	467 s	472 s	455 s	468 m	439 m	469 m	467 m	
16055	10638 , 15243 , 19300	11000 , 15225 , 29000	17100	15650	15386 , 21146	15612	16790	16000 , 21100	15677	15755	15984 , 20835	17301

P- ISSN 1991-8941 E-ISSN 2706-6703 *Journal of University of Anbar for Pure Science (JUAPS)* Open Access
2013,(7), (2) :45-51 ***2nd Conference For Pure Science - university of Anbar 20-22/11/2012***

معقدات ثلاثية النوى مع قاعدة شيف سداسية السن المشتقة من ثنائي اسيتال بارا فنلين ثنائي الامين والسالسالديهايد

خنساء شاكر النعمة

الخلاصة:

تم تحضير عدد من معقدات ثلاثية النوى مع قاعدة شيف سداسية السن H2L= (الناتج التكثيفي لثنائي اسيتايل ثنائي بارا فنلين ثنائي الامين والسالســـــالديهايد). المعقـــدات المحضـــرة ذوات الصـــيغ [M2M-(H2L)2CL4]Cl2 و [M2M-(L)2]CL2 حيـــث M=Co(II),Ni(II)، M-،Cu(II) Zn(II)= Cd(II), Hg(II), H2L. و L قاعدة شيف المتعادلة وثنائية القاعدة حضرت المعقدات عن طريق تفاعل املاح كلوريدات العناصر مع الليكاند وفي الوسطين المتعادل والقاعدي . درست المعقدات المحضرة والليكاند بالطرق الفيزياوية والكيمياوية والطيفية. وقد اتضح من الدراسة بان قاعدة شيف تسلك سلوك ليكاند سداسي السن متعادل وسداسي السن ثنائي القاعدة من خلال ذرات نتروجين الايزوميثين وذرات الاوكسجين الفينولية . واقترحت الدراسة بنية ثماني السطوح والمربع المستوي للذرتين الجانبيتين في المحيطين المتعادل والقاعدي على التوالي وان الذرة الوسطية ذات تناسق رباعي وفي جميع المعقدات.