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

Khansa S.AL - Numa
Mosul University - College of Science

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 [$M_2M^-(H_2L)_2\ Cl_4]Cl_2$ 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 .

Key words : diacetyl ; Schiff base ; salicylaldhyde ; trinuclear ; hexadentate .

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

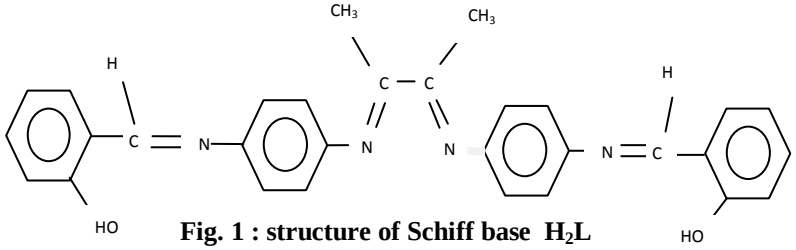


Fig. 1 : structure of Schiff base H_2L

Experimental :

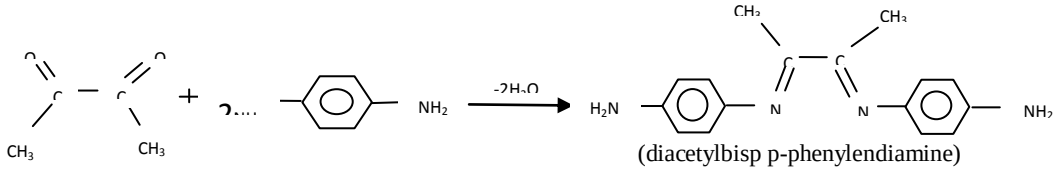
All chemicals used were of high purity (BDH or Fluke) , Melting point were determined using Buchi 510 melting point apparatus . Infrared spectra were recorded using Tensor 27 Co. Bru Keo (FT,IR) spectrophotometer 400 – 4000 cm-1 as KBr disc . The electronic spectra were recorded on Schimadzu UV. Visible spectrophotometer UV-160 for 10-3M solution of complexes in DMSO at 25 C0 . 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 spectrophotometrically 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 (2x3 ml) and ether (3 ml) then dried in air , as shown in the following equations .

Step 1:



(diacetylbisp p-phenylendiamine)

Step 2:

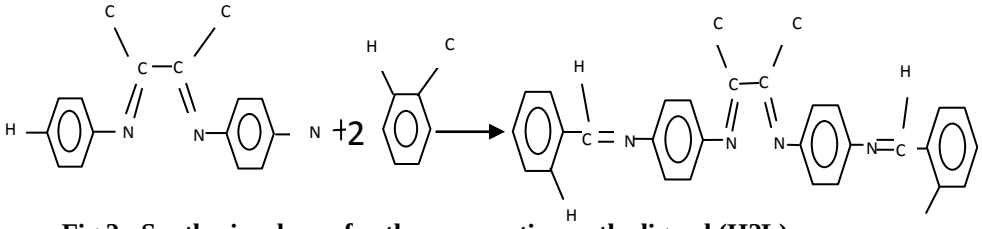


Fig 2 : Synthesis scheme for the preparatio.. of the ligand (H2L)

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 $ZnCl_2$.(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] .

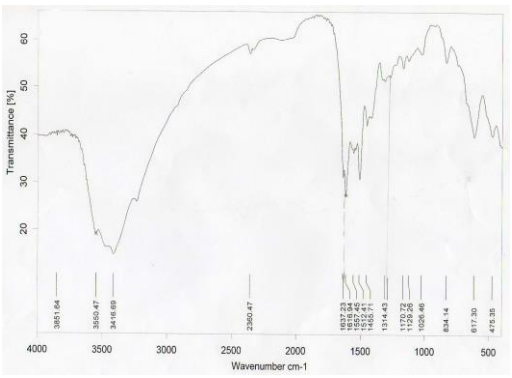
For type – I – complexes room temperature magnetic moment of Co(II) complexes (1,4,7) , are 4.80 – 4.87 B.M .The electronic spectrum shows bands at 10500 – 11100 , 14206 – 15243 and 18656 – 19300 Cm^{-1} . Thus the spectra resemble those of complexes possessing octahedral geometry[18, 19] . Assuming 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] .

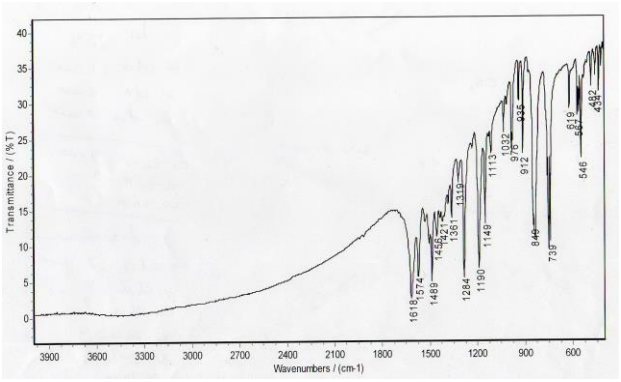
The Ni(II) complexes (11, 14 , 17) show a diamagnetic moment [23] and the electronic spectra of these complexes show bands at 15386 – 16000 cm^{-1} and 24600 – 26550 cm^{-1} which are assignable to $^1A_1g \rightarrow {}^1A_2g$ and $^1A_1g \rightarrow {}^1B_1g$ which is consistent with square planar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

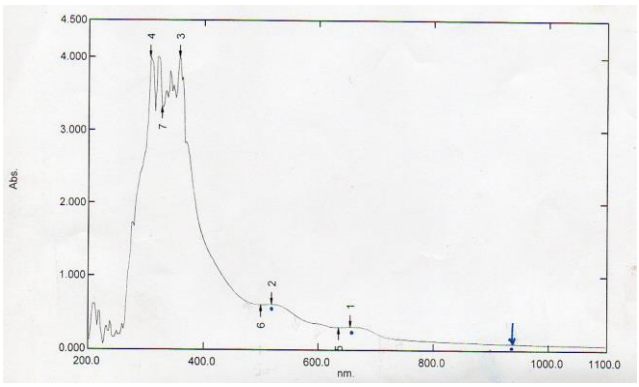
According to the above measurements ,we suggest the following structures of complexes as in (Fig . 7) .



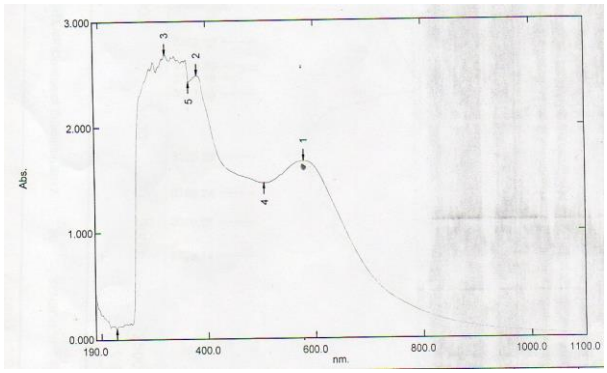
(Fig . 3) IR. Spectra for (H_2L)



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



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



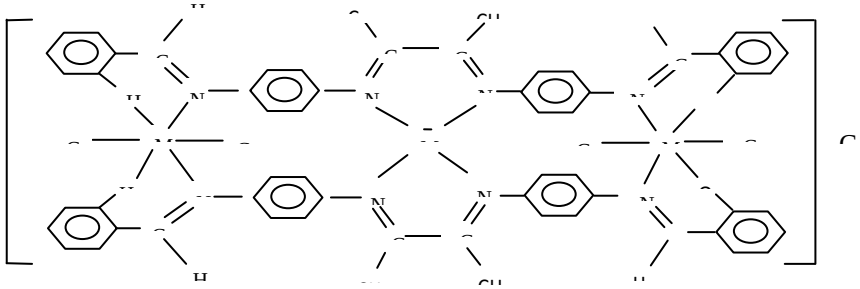
(Fig . 6) UV. Spectra for complex (18)

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

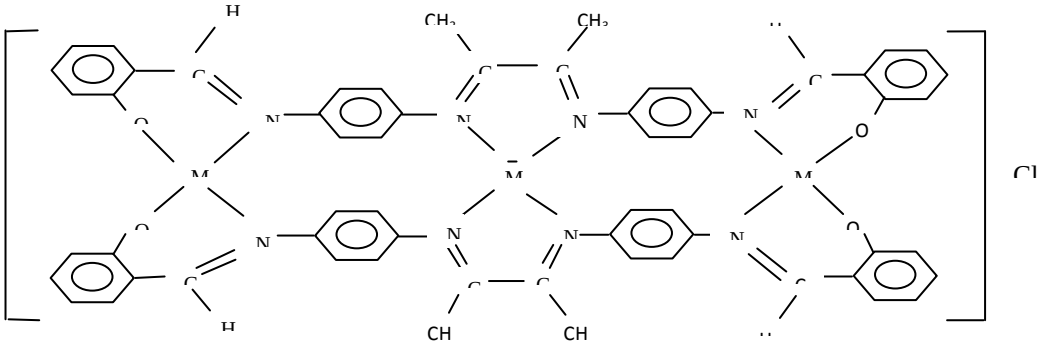
NO.	Complexes	Color	m.p (^{0}C)	Cond.Λ ohm^{-1}cm^2.mol^{-1}	Meff B.M	M%Calc. (found)
1	[Co_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Greenish yellow	160	72.5	4.80	8.76 (9.26)
2	[Ni_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Brown	178	75.0	2.85	8.74 (9.11)
3	[Cu_2 Zn $(H_2L)_2$ Cl_4] Cl_2	Dark green	192	69.8	2.15	9.38 (9.98)
4	[Co_2 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)

Table 2 : I.R . spectra (cm-1) and electronic spectra (Cm-1) of the ligand and their complexes **s = stong ; m = medium ; w=weak**

Comp.	ν (C=N)	ν (OH)	ν (C-O)	ν (M-O)	ν (M-N)	Electronic spectra (Cm^{-1})
H_2L	1637 s	3550 m	1279 w	-	-	
1	1612 s	3410 m	1326 w	500 s	433 s	10500 , 14947 , 18656
2	1610 s	3430 m	1300 w	500 s	470 s	10000 , 15300 , 23750
3	1617 s	3415 m	1298 m	500 s	471 s	1600
4	1615 m	3419 m	1295 m	515 m	430 m	11100 , 16100 , 19300
5	1609 s	3428 m	1318 m	510 m	432 s	10893 , 14205 , 24752
6	1612	3400 w	1320 m	520 m	466 s	16055
7	1615 m	3410 m	1315 m	503 s	450 m	10638 , 15243 , 19300
8	1607 s	3402 m	1300 m	518 s	472 m	11000 , 15225 , 29000
9	1615 m	3426 w	1291 m	514 s	475 s	17100
10	1610 s		1311 m	520 s	460 s	15650
11	1611 s		1298 w	532 s	467 s	15386 , 21146
12	1616 s		1301 m	512 s	472 s	15612
13	1612 m		1322 m	510 m	455 s	16790
14	1609 m		1310 s	548 m	468 m	16000 , 21100
15	1618 s		1319 w	546 m	439 m	15677
16	1610 m		1324 w	550 m	469 m	15755
17	1608 s		1320 m	516 m	467 m	15984 , 20835
18						17301



(Type – I -)



M = Co , Ni , Cu ; M^{-} = Zn , Cd , Hg

(Type – II -)

Fig . 7 proposed structures for the prepared complexes

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

خنساء شاكر النعمة
E.mail: dean_coll.science@uoanbar.edu.iq

الخلاصة:

تم تحضير عدد من معقدات ثلاثية النوى مع قاعدة شيف سداسية السن H2L = (الناتج التكثيفي لثنائي اسيتايل ثنائي بارا فنلين ثنائي الامين والسالسالديهايد) . المعقدات المحضرة ذوات الصيغ [M2M-(H2L)2 CL4] Cl2 و [M2M-(L)2]CL2 حيث Co(II) , Ni(II)= M- , Cu(II) , Zn(II)= M- , 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