New Bidentate Schiff-Base Complexes Derived from 4-Hydroxy benzaldehyde with Semicarbazide Urea and thio Urea

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Abstract

Three types of Schiff-base have been prepared derived form 4-hydroxy benzaldehyde with semicarbazide , urea and thio urea L_1, L_2, L_3 respectively. All these were bidentate ligands reacted with Fe (II), Co(II) & Ni(II) ions in 1:2 metal to ligand molar ration to form $[M(L)_2Cl_2]$ complexes.

The complexes have been characterized by means of metal analysis M%, IR, UV-Visible spectroscopy and magnetic moment measurement as well as the molar conductivity measurements .

Introduction

Urea and its derivatives have been widely used to prepare a good deal and different types of schiff bases, and their complexes. (1,2,3). This is may due to their capability of acting as multi-dentate ligand with N,O,S doner atoms(4,5,6). Halit. etal and Hua. etal prepared a microcyclic ligand with 18-memberd and 36-memberd schiff base which can be reacted with some transition metal ions to form new complexes. All these complexes characterize by single crystal X-ray and different physical tests like IR, Uv-Visible H NMR and CHN, which have different geometries. (1, 7)

On the other hand, Schiff base coordination compounds , are of considerable importance in the field of metal enzymes and homogenous catalysis biological and industrial applications (8). In view of the above our interest turned toward the investigation and the interaction between some of the first transition metal ions and three donating schiff- base ligands Fig (1) .

Experimental

The three Schiff-bases ligand L_1, L_2 and L_3 Fig (1) were prepared by dissolving 4-hydroxy benzaldehyde (2.44g, 0.02mol) in ethanol ($15cm^3$) followed by addition of (0.01 mol). Urea, thio urea and semicarbazide after adding (0.5 ml) glacial acetic acid, the mixture was refluxed for 3h. This was then cooled in ice bath and a precipitate started to deposit. The solids was filtered off and washed with cold ethanol and dried under vacuum(9). The same procedure was followed to prepare L_2 by using (7.8g, 0.01mol) of thiourea and L_3 by using (7.5g, 0.01mol) of semicarbazide respectively as shown in Fig (1) .

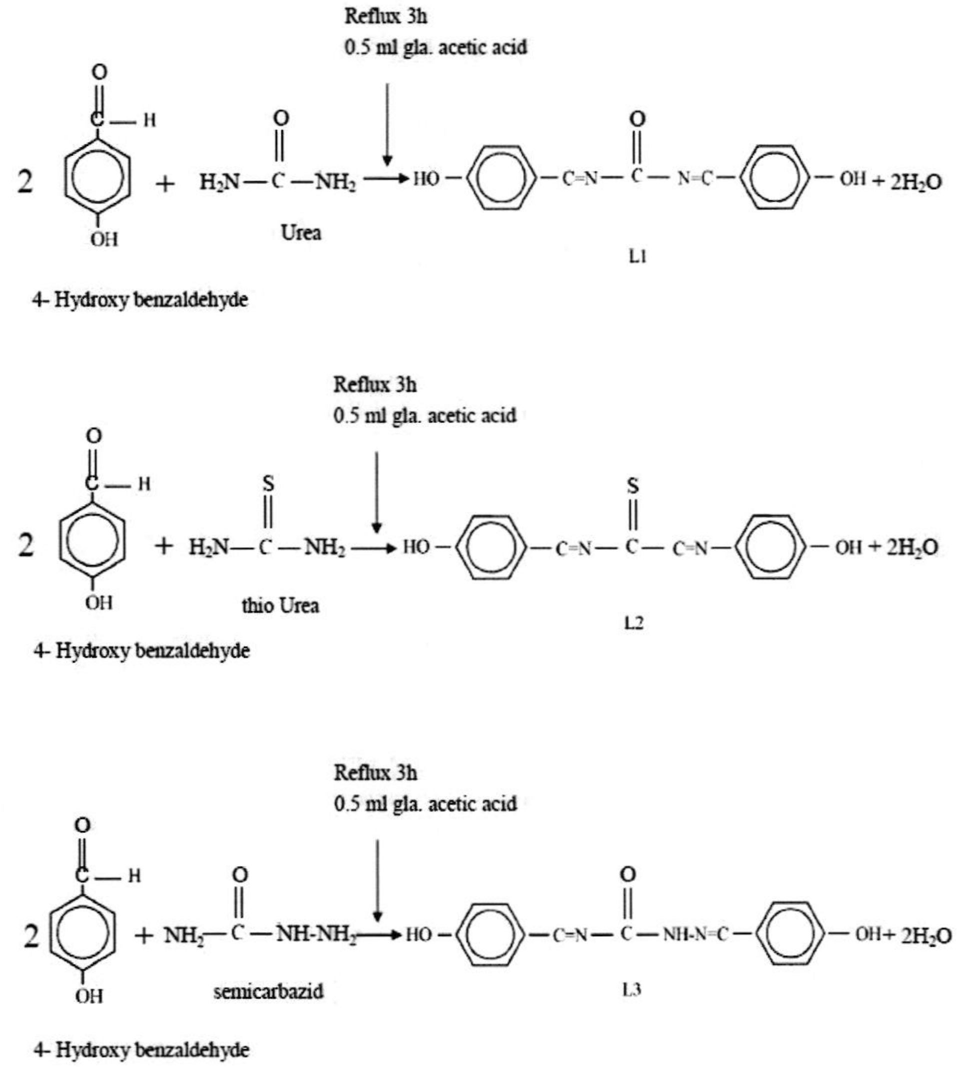


Fig (1) : Preparation and structure of the ligands L_1, L_2, and L_3

A: preparation of the metal complexes

Preparation of [Co $(L_1)_2$ Cl_2] complex

A hot ethanolic solution of the ligand L_1, L_2 L_3 (0.002mol) and ethanolic solution of hydrated metal ions (II) Chloride salt (0.001mol) in 20 ml ethanol were mixed together in 2:1 ligand: metal ions molar ratio with stirring, the mixture was refluxed for 1h, on cooling a gray precipitate was formed, filtered off washed with cold ethanol and dried under vacuum. Some physical measurements are listed in Table (1).

B: physical measurements

Metal content analysis of the complexes were carried out using standard method. Infrared spectra in the range 4000-400cm^{-1} were recorded on a Perkin-Elmer 580 B spectrophotometer, as KBr dices. Electronic spectra were obtained with shimadzu UV/vis, recording UV160 spectrophotometer at room temperature, the measurement were recorded using a concentration 10^{-3}M of the complexes in DMSO. The magnetic measurement were carried out at 25°c on the solid by a Farady's method using Bruker BM6 Instrument. Conductivity were measured using a conductivity meter mod PCM 3-Jen way, these measurements were obtained by using DMSO as a solvant at concentration of 10^{-3}M at 25°c.

Result and Discussion

The spectrum of the ligands L_1, L_2 and L_3 have bands in the U.V region at (33760-41871cm^{-1}) assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. The complexes and the ligands are stable, non-hydroscopic and have high melting points and some of their physical properties are listed in Table (1) .

It is very important in IR spectra of the ligand and complexes to notice the ν(C=N) and ν(C=O) and ν(C=S) (in L_2) absorption band to determine wither the coordination happen with N or O or S doner atoms in the ligands (L_1, L_2, L_3) with the Fe (II) Co(II), Ni (II) ions. The down shift of the ν(C=N) absorption band at (1517-1556 cm^{-1}) for L_1 complexes, (1501-1525 cm^{-1}) for L_2 complexes and (1561-1585 cm^{-1}) for L_3 complexes were observed on going from the free schiff-base to their complexes Table (3), on the other hand the absorption band due to ν(C=O) appear at (1667,1684cm^{-1}) for the ligand L_1 and L_3 respectively, also shifted to lower frequencies by (20-50 cm^{-1}) on complexation, that were clearly assigned to coordination of the metal to ligands Via. N- azo (10), and may coordinate through C=O in the same molecule or with other neighboring molecule. The ν(C=S) for the ligand L_2 appear at 834cm^{-1}, did not change in the spectra of the complexes number (2, 5 and 8) which also assist the coordination through the N and not throw the S (11).

Some other new band appeared in 412- 466cm^{-1} reign in the IR spectra of the complexes which were not present in the spectrum at the ligands, maybe attributed to νM-N , also band appeared at 450-472cm^{-1} for the complexes number (1, 4, 6, 7 and 9). May attributed to νM-O assigned to coordination of C=O group.

Magnatic and Electronic spectra Measuurment

Cobalt (II) Complexes

The cobalt (II) complexes number 1, 2 and 3 possess a magnetic moment value 4.88, 4 .81 and 4.86 B.M respectively corresponding to three unpaired electron of octahedral structure, the high values may due to orbital contribution, The U.V- visible spectra data show, a three band ^4T_1g (F)→^4T_2g (F) $ν_1$, ^4T_1g →^4A_2g ($ν_2$) and ^4T_1g (F)→^4T_1g (p) $ν_3$ respectively as shown in Table (2) in accordance with other similar complexes(12, 13 , 14).

Nickel (II) Complexes

The magnetic moment values of the nickel (II) complexes (4, 5 and 6) have 3.19, 3.02 and 3.11 B. M at room temperature respectively, these values may attributed to octahedral environment around Ni (II) ions (15).

The U.V- visible spectrum shows three bauds attributed to ^3A2g (F)→$^3T2g(F)$ $ν_1$, $^3A2g(F)$→T1g(F) $ν_2$ and^3A2g (F)→3T1g (p) $ν_3$.

Transition are in accord to the octahedral geometry (11, 15).

Iron (II) complexes

The magnetic moment values of the complexes number 7, 8, and 9 4.92, 4.90 and 4.76 B.M respectively, were well in accord with those having octahedral structure (10, 14).

The electronic spectra at room temperature showed a bands at 19230 and 17543cm^{-1} attributed to (^5T_2g →^5Eg) transition and could be a distorted octahedral structure. The conductivity values of those complexes were in accord with their tentative structure (11, 15) Table (1)

On the basis of the above discussion we propose the following structures for the metal (II) complexes as in Fig (2) .

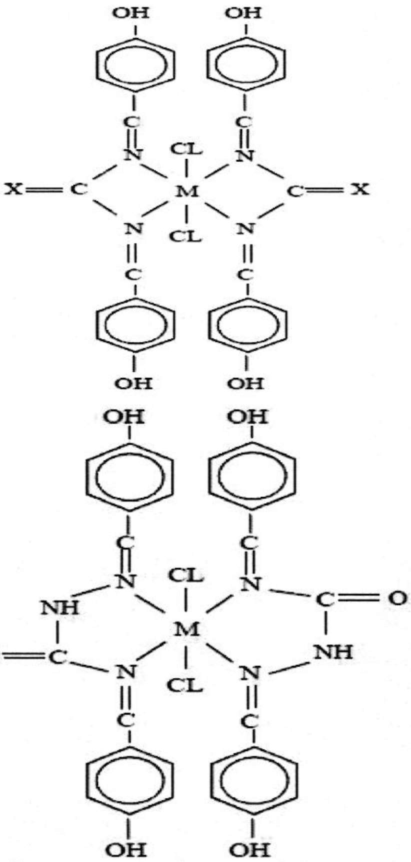
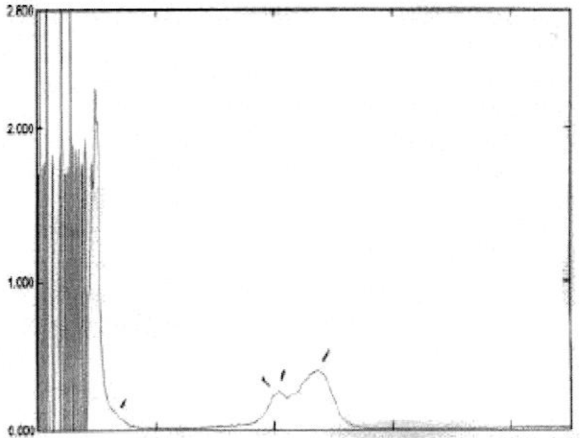
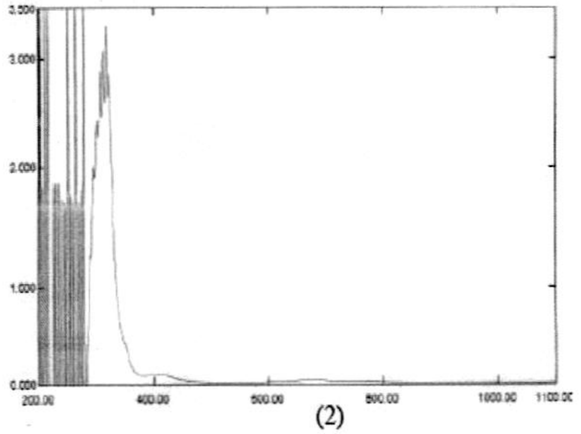


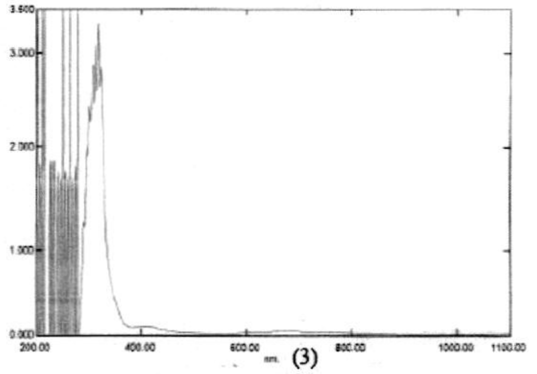
Figure 2: suggested strictures of the complexes where: M= Co (II) , Ni(II) and Fe(II), X=O or S



(1)

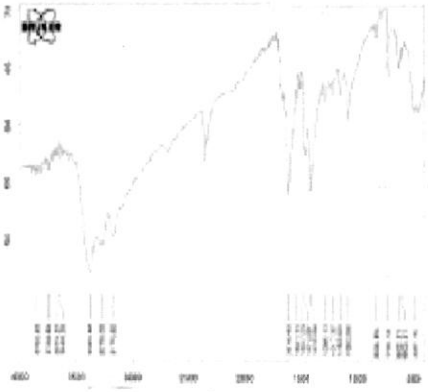


(2)

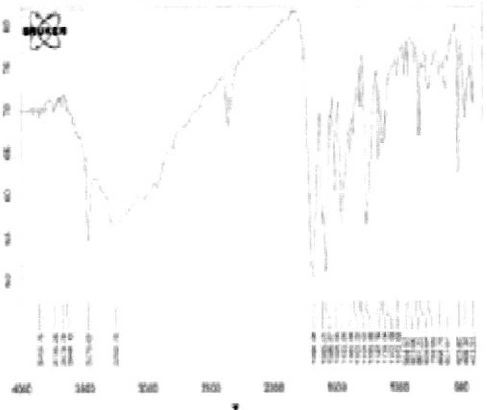


(3)

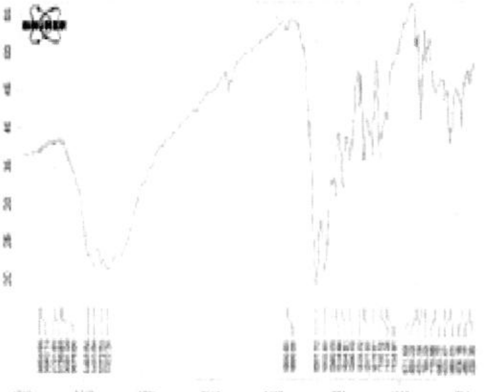
Figure 3: Uv-Visible chart's for 1-[Co $(L_2)_2$ Cl_2], 2-[Ni $(L_1)_2$ Cl_2], 3-[Fe $(L_2)_2$ Cl_2] complexes



L_1

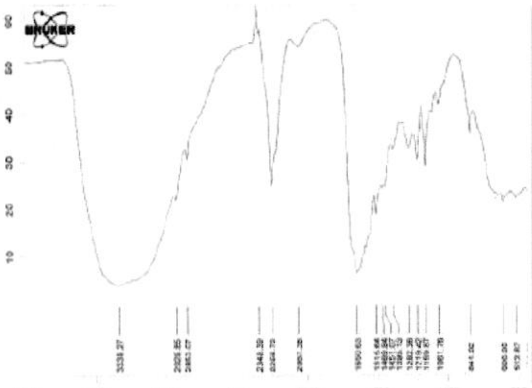


L_2

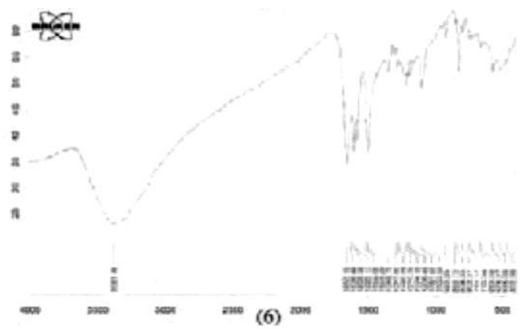


L_3

Figure 4: IR-Spectra chart's for L_1, L_2 and L_3 ligand



(3)


(6)

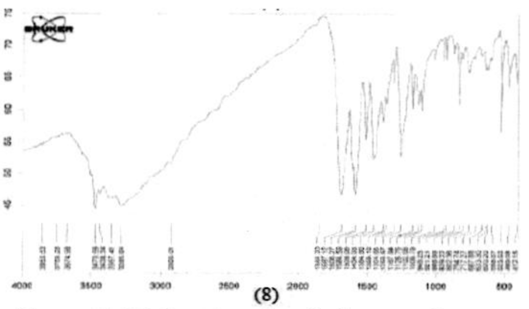

(8)

Figure 5: IR-Spectra chart's for complexes number 3, 6 and 8

Table (1): Molar conductance and M % and some physical data of the compounds

No	Compound	Color	M.P (°c)	Yield%	Molar conductance $(\Omega^{-1}cm^2mol^{-1})$	mental % found (calculated)
	L1	اخضر فاتح	171-173	80		
	L2	ابيض	165-167	85		
	L3	اصفر فاتح	205-207	78		
1	$[Co(L_1)_2Cl_2]$	رصاصي فاتح	95	80	19	(8.89) 8.48
2	$[Co(L_2)_2Cl_2]$	(أخضر مزرق)	186	75	34	(8.48) 8.28
3	$[Co(L_3)_2Cl_2]$	اصفر فاتح	220	79	11	(8.51) 8.21
4	$[Ni(L_1)_2Cl_2]$	أخضر غامق	190	83	11	(8.87) 8.65
5	$[Ni(L_2)_2Cl_2]$	قهوائي مخضر	146	76	10.8	(8.46) 8.27
6	$[Ni(L_3)_2Cl_2]$	اخضر فاتح	217	80	17	(8.48) 8.39
7	$[Fe(L_1)_2Cl_2]$	قهوائي	190	78	44	(8.49) 8.40
8	$[Fe(L_2)_2Cl_2]$	قهوائي	علكي	76	18.6	(8.10) 8.08
9	$[Fe(L_3)_2Cl_2]$	قهوائي غامق	195	77	17.6	(8.12) 7.95

Table (2): Magnetic moment and electronic spectral data of the complexes

No	compound	Meff B.M (25°C)	λ max (cm^{-1})
	L1	------	33825-38790
	L2	------	35610-41871
	L3	------	33760-38821
1	$[Co(L_1)_2Cl_2]$	4.86	16666, 16420, 14836, 33333
2	$[Co(L_2)_2Cl_2]$	4.81	16949, 14814, 16420, 33444
3	$[Co(L_3)_2Cl_2]$	4.86	14947, 16447, 16806, 30864
4	$[Ni(L_1)_2Cl_2]$	3.19	13280, 14705, 24449, 31348
5	$[Ni(L_2)_2Cl_2]$	3.02	13157, 14577, 24096, 32573
6	$[Ni(L_3)_2Cl_2]$	3.11	14749, 31152, 32289
7	$[Fe(L_1)_2Cl_2]$	4.92	17543, 31152, 34345
8	$[Fe(L_2)_2Cl_2]$	4.90	17543, 32157, 37932
9	$[Fe(L_3)_2Cl_2]$	476	19230, 314521, 36041

Table (3): Selected IR bands and their assignment in cm^{-1}

No	compounds	ν(C=O)	ν(C=N)	ν (N-N)	ν (M-O)	ν(M-N)	ν(C=S)
	L_1	1667	1602				
	L_2		1616				834
	L_3	1684	1605	1011			
1	$[Co(L_1)_2CL_2]$	1647	1541		450	419	
2	$[Co(L_2)_2CL_2]$		1501			466	833
3	$[Co(L_3)_2Cl_2]$	1687	1584	1009		412	
4	$[Ni(L_1)_2 Cl_2]$	1647	1517		458	419	
5	$[Ni(L_2)_2 Cl_2]$		1525			415	834
6	$[Ni(L_3)_2 Cl_2]$	1667	1585	1010	472	433	
7	$[Fe(L_1)_2Cl_2]$	1643	1556		456	435	
8	$[Fe(L_2)_2Cl_2]$		1525			428	841
9	$[Fe(L_3)_2Cl_2]$	1636	1561	1009	454	419	

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تحضير معقدات جديدة لقواعد شيف ثنائية السن مشتقة في 4- هيدروكسيد بنزلديهايد والسيكاربازايد واليوريا والثايويوريا

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الملخص

تم تحضير ثلاثة انواع من قواعد شيف مشتقة من 4- هيدروكسي بنزالديهايد مع السيمكاربازايد او اليوريا او الثايويوريا L_1 و L_2 و L_3 على التوالي لقد كانت هذه الليكاندات ثنائية السن حيث تناسقت مع الحديد (II) والكوبلت (II) والنيكل (II) وبنسب مولية 1: 2 لتكون الصيغة العامة $[M(L)_2 Cl_2]$. تم تشخيص هذه المعقدات باستخدام التحليل الدقيق للمحتوى الفلزي M% وطيف الاشعة تحت الحمراء والمرئية – فوق البنفسجية والقياسات المغناطيسية اضافة إلى قياسات الموصلية الكهربائية المولارية .