Vol. 29 (1) 201**6**

Synthesis and Characterization of [Benzyl (2-hydroxy-1naphthylidene) hydrazine carbodithioate] and Its Metal Complexes With [Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] Ions

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Abstract

The formation of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)-complexes (C1-C5) respectively was studied with new Schiff base ligand [benzyl(2-hydroxy-1-naphthalidene) hydrazine carbodithioate derived from reaction of 2-hydroxy-1-naphthaldehyde and benzyl hydrazine carbodithioate. The suggested structures of the ligand and its complexes have been determined by using C.H.N.S analyzer, thermal analysis, FT-IR, U.V-Visible, ¹HNMR, ¹³CNMR, conductivity measurement, magnetic susceptibility and atomic absorption. According to these studies, the ligand coordinates as a tridentate with metal ions through nitrogen atom of azomethane, oxygen atom of hydroxyl, and sulfur atom of thione and the ratio of ligand to metal (M:L) as (1:2) all the complexes were octahedral except copper-complex was distorted octahedral.

Key words: Schiff base ligand.

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

Introduction

Schiff bases are typically formed by the condensation of a primary amine and an aldehyde or ketone. Schiff bases are generally bidentate, tridentate, tetradentate or polydentat ligands [1]. The type of aliphatic Schiff's bases are relatively unstable in aqueous acid or base solution where hydrolyzed back to their aldehydes or ketones and amines, while aromatic counterparts are stable due to the resonance [2,3]. Schiff bases are the significant compounds owing to their wide range of biological activities and industrial applications [4]. Benzyl hydrazinecarbodithioate (SBDTC) is interesting due to the fact that its derivatives have the potential to be modified in various ways by introducing several different substituents [5]. 2-Hydroxy Schiff base ligands are very important due to the existence of (O-H…N and N-H…O) type hydrogen bonds tautomer's between of enolimine and keto-enamine forms [6]. The spectra of different Schiff -bases have been studied in polar and nonpolar solvents and mixed solvents, it was established that the tautomeric equilibrium in 2-hydroxy-1-naphthylidene aniline Schiff bases depend on the polarity of the solvent, the acidity of the medium, the temperature and the strength of the hydrogen bond[7]. Schiff bases are used in drug. It is well known that the shape of a certain molecule is the most important factor that affects drug activity. The four major factors that affect the properties of a drug are: its ability to chelate with metal ions, its lipophilicity, steric effects and electronic effects [8]. This paper reports the synthesis and characterization of new Schiff base ligand derived from reaction 2-hydroxy-1naphthaldehyde and benzyl hydrazine carbodithioate and its complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Experimental

Materials and instruments

All reagents and solvents are of highest purity and used as obtained from the manufacture. Melting points were determined by using (Gallenkamp melting point apparatus) at Baghdad University. U.V-Vis. Spectra were performed in a mixture of ethanol and acetone (2:1) on a (Shimadzu UV-1800) in the range (200-1100) nm at Baghdad University. IR-Spectra were recorded on a (Shimadzu FTIR- 8400s) in the range (400-4000)cm⁻¹ using KBr disk, and (250-4000) cm⁻¹ using CsI disk at Baghdad University . The ¹HNMR spectra were gained on the (Advance III 400 Bruker 400 MHz) using DMSO as solvent at Iran / Isfahan University. The element analysis (C.H.N.S) was gained on a (Euro EA 3000) at Ibn Al- Haitham, Baghdad University. Thermal analyses (TG-DTG) were gained on a (Shimadzu 60-H Thermo Gravimetric Analyzer) at college of Education for Pure Science Ibn Al- Haitham, Baghdad University. Atomic absorption spectroscopy was gained on a(GBC 933 plus Absorption Spectrophotometer) at Bagdad University. Molar conductivity measurements (at conc. 10⁻³M) in DMSO were carried out by using Hunts capacitors Trade Mark British at Bagdad University. Magnetic susceptibility were gained on the Auto Magnetic Susceptibility Balance Model Sherwood Scientific) at Al-Mustansiriyah University.

Vol. 29 (1) 2016

Ibn Al-Haitham Jour. for Pure & Appl. Sci. Vol. 29 Synthesis of Schiff base ligand [benzyl(2-hydroxy-1-naphthyldiene) hydrazine carbodithioate]

A solution of (0.99gm, 0.005 mole from benzyl hydrazine carbodithioate (SBDTC) in (35ml) of hot ethanol (99.9%) was added to solution of 2-hydroxy-1-naphthaldehyde (0.86gm ,0.005 mole) in (35ml) of hot ethanol (99.9%). The mixture was heated with stirring (reflux 6h), then the mixture was cooled in IC-bath to complete the recrystallization. The yellow product was washed in cold ethanol and recrystallized and dried overnight in vacuum desiccator that contains silica gel (yield 70%, m.p. 204-206°C) as shown in Scheme(1)[9].



Synthesis of complexes

The mole ratio of synthesis complexes was (1:2)(M:L). Schiff base L (0.176 gm ,0.0005 mole) was dissolved in mixture of acetone and absolute ethanol (20 ml of ethanol + 10 ml of acetone) and heated at 70 °C with stirring until became clear solution. A half mole of metal salts [as acetate in cobalt(II)(0.0622gm),zinc(II)(0.0548gm), and cadmium(II)(0.0665gm), as chloride in nickel (II)(0.059gm) and copper(II)(0.0606gm)] was dissolved in absolute ethanol (10ml) and heated. Both solutions were mixed together and heated with stirring (reflux 10 h). Then the mixture is allowed to cool and the precipitate formed filtered off.

Results and discussion

The Schiff base ligand was prepared by the condensation reaction. The element microanalysis data of the prepared (L) and its complexes with [Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] ions are in good convention with the calculated results from expected formula of each synthesized compounds as listed in table(1).

Thermal analysis of L and its metal complexes

The first stage of mass-lose is resulted in the temperature ranges (140-430),(180-455),(160-290), (165-315),(80-210), and (180-310) °C were defined for the ligand (L) and its complexes (C₁,C₂,C₃,C₄, and C₅) respectively. As evidenced from calculated and observed mass-loss, where, the first stage of mass-loss to confirm the existing of water hydration and solvent molecules. The final stage of mass-loss in the thermal decomposition of some complexes gave oxides or sulfide as final residue depending on the altimetry between the metal and binding atom of the ligand. This refers to the stability of these oxides or sulfides within the decimate temperatures range. The ligand and its complexes are stable at room temperature. The thermal analyses data of ligand and its complexes were listed in the table (2). The Thermograph of the ligand(L) and its Co-complex(C₁) are shown in the figures(1 and 2).

Ibn Al-Haitham Jour. for Pure & Appl. Sci. **Spectroscopic Characterization**

FT-IR Spectra

The FT-IR spectra of synthesized ligand and its synthesized complexes were recorded in (KBr) and (CsI) disk . The IR spectrum of ligand (L) was showed a sharp absorption band at (1622.02 cm⁻¹) which attributed to stretching vibration of v(C=N) which was shifted to (1616.24, 1616.24, 1616.24, 1620.21.and 1618.17cm⁻¹) in the (C₁-C₅) respectively[10,11]. The weak band appeared at (1083.92cm⁻¹) is assigned to vibration of v (C=S)[12,13]. IR spectra of complexes show no more v(N-H) peak but do no exhibit a v(C=S) band since the thiones groups was relatively unstable in the monomeric forms and have a tendency to change into more stable thiol form by enethiolization process[14]. However they show v(C-S) band at around (975.91-1000.00)cm⁻¹. These indicate that the complexation occurred between Schiff base and metal ion in the solid state, the ligand remains in the thione form. The sharp and strong band appeared at $(1319.22 \text{ cm}^{-1})$ which is attributed to vibration of v (C-N) of the ligand which was shifted to (1336.58 cm⁻¹ with shoulder in C₁, 1338.51 cm⁻¹ and became weak in C₂, 1336.56 cm⁻¹ in C₃, 1330.88 cm⁻¹in C₄, and 1325.01 cm⁻¹ in C₅) [15]. The weak band appeared at $(3028.03 \text{ cm}^{-1})$ was attributed to vibration of v (NH) in the ligand [16], while absorption bands appeared at $(528.46-553.51 \text{ cm}^{-1})$ were attributed to υ (M-N) for C₁-C₅ respectively[6,17]. The absorption bands appeared at (374-383 cm⁻¹) were attributed to stretching vibrations of v (M-S) for C1-C5 respectively [18,19]. The absorption bands appeared at (450-478cm⁻¹) were attributed to stretching vibrations of v (M-O) for C₁-C₅ respectively [1]. While the weak absorption bands appeared at $(3409.91-3446.56 \text{ cm}^{-1})$ were assigned to $v(H_2O)$, v (OH) [5,20]. The IR spectra of ligand and its Co-complex (C₁) are shown in the figures(3and 4) and the data listed in the table(3).

Molar Conductance

The molar conductance of all synthesized complexes were measured in DMSO at room temperature. The values obtained lie in the range (3.3-24.0 S.cm².mol⁻¹), these indicate that all the synthesized complexes are non-electrolyte. The data of molar conductance were listed in the table(4).

Magnetic Susceptibility

According to the magnetic moment values, all synthesized complexes are paramagnetic except complexes (C_4 and C_5) are diamagnetic because the Zinc and Cadmium ions have filled *d*-orbital. The data of magnetic susceptibilities were listed in the table(4).

Electronic Spectra

The UV-Vis. Spectra of the ligand and its metal complexes were established in mixed of ethanol and acetone (2:1) at (10⁻⁴M) at room temperature in the region (200-1100)nm. The ligand showed bands at (265,335) nm assign to ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) transitions, which are shifted to [(263,311), (291, 326), (273, 327), (266, 334), and (320)] nm in C₁-C₅ respectively[16,22]. In addition the ligand spectrum showed three high intensity bands appeared in the near Visible region at (381,400,and 475) nm were assigned to intra-ligand charge transfer (ILCT), which are shifted to [(411,434,464), (406,430), (418), (415), (410)] nm in the(C₁-C₅) respectively [21,23]. While C₁ appeared bands at (709, 787, 806) nm, C₂ appeared three bands at (544, 592,and 649) nm, and C₃ appeared band at(680)nm and these bands were attributed to d-d transitions[17,18,22]. There is no d-d transition in C₄, and C₅

Ibn Al-Haitham Jour. for Pure & Appl. Sci.

because of fill d-orbital in the Zn and Cd ions. The electronic spectra of the ligand and its Cocomplex (C_1) were shown in the figures (5 and 6) and their data were listed in table(4).

The NMR Spectra

¹HNMR Spectra

The ¹HNMR Spectra for ligand and its (Zn(II)-L) (C₄) complex were registered in DMSO as solvent. The free ligand showed multiple peaks from $\delta(7.22-8.07\text{ppm})$ refer to aromatic ring which are shifted to δ (6.96-8.07ppm) in the C₄ [17,24,25]. The peak appeared at δ (9.2ppm) referred to the proton of azomethine group (CH=N) in the ligand that was shifted to δ (9.50 ppm) in the C₄ complex [21,25]. The peak appeared at δ (4.60ppm) was attributed to chemical shift of S-CH₂ proton for ligand and shifted to $\delta(4.41 \text{ ppm})$ in the C₄ complex [4,16]. The peak appearance of a signal at δ (11.08 ppm) attributed to OH⁻ aromatic for ligand that sifted to δ (10.00 ppm) in the C₄complex[14, 25]. The peak appeared at δ (13.50 ppm) was attributed to NH group for ligand [4,26,27]. The ¹HNMR of complexes show no more v(N-H) peak but do no exhibit a δ (C=S) band since the thiones groups was relatively unstable in the monomeric forms and have a tendency to change into more stable thiol form by enethiolization process[14]. The weak peak appeared at δ (2.09 ppm) and sharp peak appeared at δ (1.91ppm) refer to CH₃ of ethanol in ligand and its Zn-complex, and the peak appeared at $\delta(3.42-3.6)$ ppm refer to protons of H₂O of moisture for DMSO in the ligand and refer to water molecule in the Zncomplex, the peak appeared at $\delta(2.51-2.68)$ ppm referred to the solvent [28,29]. The ¹HNMR spectrum of (L) and its Zn-complex (C₄) are shown in the Figures (7 and 8) and listed in the table (5).

¹³CNMR Spectra

In the free ligand, the aromatic carbons appeared in the range $\delta(109.13-136.90 \text{ ppm})$ which were shifted to $\delta(106.96-138.65\text{ppm})$ in the C₄ [30,31]. The peak appeared at $\delta(158.27\text{ppm})$ referred to the C-OH for naphthalene ring for ligand which was shifted to $\delta(162.50\text{ppm})$ in the C₄, the azomethine group appeared a peak at $\delta(146.09 \text{ ppm})$ in the ligand which was shifted to $\delta(154.30\text{ppm})$ in the C₄ [4,16]. The peak appeared at $\delta(194.42\text{ppm})$ in the ligand which referred to $\delta(C=S)$. The peak appeared at $\delta(172.15\text{ppm})$ which was assigned to $\delta(C-S)$ in the C₄ [4,30].The methyl carbons of the ligand appeared at $\delta(37.45\text{ppm})$, which was shifted to δ (34.18 ppm) in the C₄ [4].The peak appeared at $\delta(39.23-40.08 \text{ ppm})$ was corresponded to the solvent peak (DMSO). The ¹³CNMR spectra for (L) and its Zn-complex (C₄) were shown in the Figures (9 and 10) and listed in the table (6).

According to the spectral data and measurements mentioned above of the synthesized complexes, the suggested structures of these complexes (C_1, C_2, C_4 and C_5) were concluded as octahedral geometry except copper-complex(C_3) was appeared as a distorted octahedral as shown in figures(11-15).

Conclusion

The Schiff base (L) was found to be linked with [Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] ions through nitrogen atom of azomethane group, sulfur atom of thiocarbonyl, and oxygen atom of hydroxyl group. The chemical structure for the ligand and its complexes have been studied by different physiochemical techniques FTIR, NMR, UV-Vis spectroscopies, thermal analysis ,atomic absorption, conductivity measurements, magnetic Susceptibilities and element analysis were gave a results corresponding to mole ratio of (2:1) and the structures of the

Vol. 29 (1) 2016

Ibn Al-Haitham Jour. for Pure & Appl. Sci. synthesized complexes was octahedral geometry expect the Cu-complex was distorted octahedral geometry.

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Vol. 29 (**1**) 201**6**

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Sym.	Color	Decom.	%Yield	% Element Analysis Found (Cal.)				
		Temp. (m.p.)⁰C		%C	%Н	%N	%S	. % Metal Found (Cal.)
L	yellow	204-206	70	63.98	4.79	7.76	16.80	-
				(63.33)	(5.52)	7.03	16.08	
C ₁	brown	186	68	59.43	4.41	6.88	13.29	7.15
				(59.02)	(4.28)	(7.06)	(16.14)	(7.42)
C ₂	brown	>260	66	59.48	4.03	6.76	13.93	7.31
				(58.84)	(4.53)	(6.86)	(15.69)	(7.19)
C ₃	green	172	70	57.77	3.96	5.64	14.34	7.44
				(57.71)	(4.80)	(6.56)	(15.01)	(7.45)
C4	golden yellow	230	64	57.48	4.81	5.75	14.89	7.35
				(57.74)	(4.57)	(6.73)	(15.37)	(7.86)
C5	yellow	240	68	52.74	3.58	5.81	11.93	12.00
				(53.19)	(4.43)	(6.20)	(14.18)	(12.45)

Table (1): Physical properties and analytical data of ligand and its metal complexes.

المجلد 29 العدد (1) عام 2016 Ibn Al-Haitham Jour. for Pure & Appl. Sci.

Comp	Step	Temp.range of decom- position at	Peak temp_at	Suggested formula	% Mass loss	
comp.		TG °C	DTG °C	011055	Found	Cal
L	1	140-430	240	EtOH, C ₆ H ₆ CH ₂ C ₁₀ H ₆ (OH)CH	73.70	73.62
	2	430-595	540	CNHN	9.38	10.30
	3	> 595	-	S ₂	16.91	16.08
C ₁	1	180-455	234.8	0.5 EtOH, 0.5H ₂ O, C ₁₀ H ₆ , C ₆ H ₅ CH ₂ , C ₆ H ₅	41.67	41.11
	2	455-592	499.7	C ₁₀ H ₆ CHNNCSS,H HCNN	35.69	36.07
	3	>592		OH, CH ₂ SCS, CoO	22.63	22.94
C ₂	1	160-290	220	EtOH, 0.5H ₂ O, C ₁₀ H ₆ OH	24.55	24.15
	2	290-322	312	C ₁₀ H ₅ CH ₂ S	14.31	15.07
	3	322-455	372	C ₆ H ₅ CH ₂	11.53	11.15
	4	455-595	518	C ₆ H₅CH(OH)CHN, NCS	28.23	27.83
	5	>595	-	CHNNCS, NiS	21.42	21.53
C ₃	1	165-315	240	1.5EtOH,H ₂ O 2C ₁₀ H ₆ CH	42.18	42.82
	2	315-395	355	C ₆ H ₅ CH ₂	10.11	10.67
	3	395-595	495	C ₆ H ₅ CH ₂ SCSNN, S, C,H	28.54	28.15
	4	>595		NNS, OH ,CuO	19.19	18.36
C4	1	80-210	108	EtOH, H ₂ O C ₃ H ₃	11.63	12.39
	2	210-405	323	$C_{3}H_{2}CH_{2}, 2C_{10}H_{6}$	36.37	36.56
	3	405-590	273	C ₁₀ H ₇ SCNNCH, SCNNCH	31.38	31.39
	4	>592	183.3	OH,S ₂ ,ZnO	20.62	19.64
C ₅	1	180-310	273.4	EtOH, 2H ₂ O, C ₆ H ₅ CH ₂ C ₁₀ H ₆ CH,	34.53	34.79
	2	310-595	531.3	C ₆ H ₅ CH ₂ , HCN,NHN	24.52	24.04
	3	>595		CHNNCSS,NNCSS, OH,H, CdO	40.97	41.37

Vol. 29 (1) 201**6**





Ibn Al-Haitham Jour. for Pure & Appl. Sci.

Vol. 29 (1) 2016

Table(3): Infrared spectral data of	f ligand and its complexes.
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Comp.	υ C=N	υ C=S	υC-N	υC-S	υ H2O	υ M-N	υ M-S	υ Μ-Ο
	cm ⁻¹							
L	1622.02	1083.92	1319.22	-	3420	_	_	-
C1	1616.24	-	1336.56	987.49	3421.48	550.00	379.95	450.00
C ₂	1616.24	-	1338.51	1000.00	3446.56	553.53	383.81	470.60
C ₃	1616.02	-	1336.58	985.56	3421.48	540.03	379.95	478.31
C ₄	1620.21	-	1330.88	983.70	3433.29	536.17	374.16	464.81
C5	1618.17	-	1325.01	975.91	3409.91	528.46	360.60	462.88

Table (4): The electronic data and conductivity measurement of ligand and its complexes.

Comp	Wave	Wave no.	Assignment	Molar.	μeff	Suggested
	length	\bar{v} (cm ⁻¹)		cond. (S.	(B.M)	Geometry
	λ(nm)	· · ·		cm ² mol ⁻¹)		
L	265	37736	$\pi { ightarrow} \pi^*$	-	-	-
	335	29851	$n \rightarrow \pi^*$			
	381	21186	IC.T			
	400	25000	IC.T			
	475	26247	IC.T			
C1	263	38023	$\pi{ ightarrow}\pi^*$	13.0	4.5	Octahedral
	311	32154	$n \rightarrow \pi^*$			
	411	24331	C.T. L→M			
	434	23041	C.T. L→M			
	464	21552	C.T. L→M			
	709	14104	${}^{4}T_{1}g(F) \rightarrow {}^{4}T_{1}g(P)$			
	787	12706	${}^{4}T_{1}g(F) \rightarrow {}^{4}A_{2}g(F)$			
	806	12406	${}^{4}T_{1}g(F) \rightarrow {}^{4}T_{2}g(F)$			
C ₂	291	24691	$\pi { ightarrow} \pi^*$	9.5	2.5	Octahedral
		23256	$n \rightarrow \pi^*$			
	326	24691	C.T. L→M			
	406	23256	C.T. L→M			
	430	18382	$^{3}A_{2}g(F) \rightarrow ^{3}T_{1}g(P)$			
	544	16891	$^{3}A_{2}g(F) \rightarrow ^{3}T_{1}g(F)$			
	592	15408	$^{3}A_{2}g(F) \rightarrow ^{3}T_{2}g(F)$			
	649					
C ₃	234	42735	$\pi { ightarrow} \pi^*$	24.0	1	distorted
	249	40161	$\pi{ ightarrow}\pi^*$			octahedral
	273	36630	$\pi{ ightarrow}\pi^*$			
	327	30581	$n \rightarrow \pi^*$			
	418	23923	C.T. L→M			
	680	14706	${}^{2}Eg \rightarrow {}^{2}T_{2}g$			
C4	266	37594	$\pi { ightarrow} \pi^*$	5.0	Diamagnetic	octahedral
	334	29940	$n \rightarrow \pi^*$			
	415	24096	C.T. L→M			
C5	320	31250	$n \rightarrow \pi^*$	3.3	Diamagnetic	octahedral
	410	24390	C.T. L→M			

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Assignment	L	Zn(L) ₂		
Ar-H	δ(7.22- 8.07ppm)	δ (6.96-8.07 ppm)		
CH=N	δ(9.20 ppm)	δ(9.50ppm)		
S-CH ₂	δ(4.60ppm)	δ(4.41ppm)		
Ar-OH	δ(11.08ppm)	δ(10.00ppm)		
CS NH	δ(13.50ppm)	-		
СНз	δ(2.03ppm)	δ(1.89ppm)		

Table (5): The ¹HNMR spectral data of ligand and its complexes.

Table (6): The ¹³CNMR spectral data of ligand and its complexes.

Assignments	L	Zn(L) ₂		
Ar-C	δ(109.13- 136.90 ppm)	δ (106.96-138.65 ppm)		
CH=N	δ(146.09 ppm)	δ(154.3ppm)		
S-CH ₂	δ(37.45ppm)	δ(34.18ppm)		
С-ОН	δ(158.27ppm)	δ(162.50ppm)		
CS	δ(194.42ppm)	δ(172.15ppm)		
CH ₃	δ (37.45 ppm)	δ (34.18 ppm)		



Figure (1): Thermograph of L.









Figure (3): The FTIR spectrum of L.



Figure (4): The FTIR spectrum of C₁.



Figure (5): The electronic spectrum for L.





Figure (6): The electronic spectrum for C₁.



Figure (7): The ¹HNMR spectrum of L.



Figure (8): The ¹HNMR spectrum of C4.

16



Figure (9): The ¹³ CNMR spectrum of L.





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Figure(11): The structure of [Co(L1)₂](0.5H₂O) (0.5 EtOH).



Figure (13): The structure of [Cu(L1)₂](H₂O)

(1.5EtOH).





Figure (15): The structure of [Cd(L1)₂](2H₂O) (EtOH).



Figure(12): The structure of [Ni(L1)2] (0.5H2O) (EtOH).



مجلة إبن الهيثم للعلوم الصرفة و التطبيقية Vol. 29 (**1**) 201**6** Ibn Al-Haitham Jour. for Pure & Appl. Sci.

تحضير وتشخيص بنزايل (2-هيدروكسي -1- نفثاليدين) هيدرازين كاربوداي ثايوات ومعقداته مع الأيونات الفلزية

[Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)]

باسم أبراهيم العبدلي نور كاظم احمد قسم الكيمياء / كلية العلوم/ جامعة بغداد استلم في:17/أيلول/2015 ،قبل في:12/تشرين الأول/2015

الخلاصة

تم تحضير معقدات للأيونات الفلزية [(II), Cu(II), Cu(II), Zn(II), and Cd(II)] مع ليكاند قاعدة شف جديدة [بنزايل (2-هيدروكسي-1- نفثاليدين) هيدرازين كاربوداي] ثايوات والمشتق من تفاعل 2-هيدروكسي-1- نفثالديهايد وبنزايل هيدرازين كاربوداي ثايوات. شخصت الصيغة التركيبية للمعقدات المحضرة وفقا للتحليل الدقيق للعناصر, التحليل الحراري, الاشعة تحت الحمراء, الاشعة فوق البنفسجية-المرئية, HNMR, ¹³CNMR, قياسات التوصيلية, الحساسية المعناطيسية و الامتصاص الذري, أذ أظهرت هذه القياسات بأن المعقدات المحضرة ذات شكل ثماني السطوح بأستثناء معقد النحاس ذي شكل ثماني السطوح المشوه. وأن النسبة بين الليكاند والايون الفلزي(M:L) هي (2:1) ويتناسق الليكاند بشكل ثلاثي السن مع الايون الفلزي من خلال ذرة النتروجين للايزوميثين وذرة الكبريت للثايوكاربون وذرة الاوكسجين لمجموعة الهيدروكسي.

الكلمات المفتاحية : ليكند قاعدة شف.